

Proceedings of the American Academy of Arts and Sciences

VOL. 79, No. 3, P. 125-179—APRIL, 1951

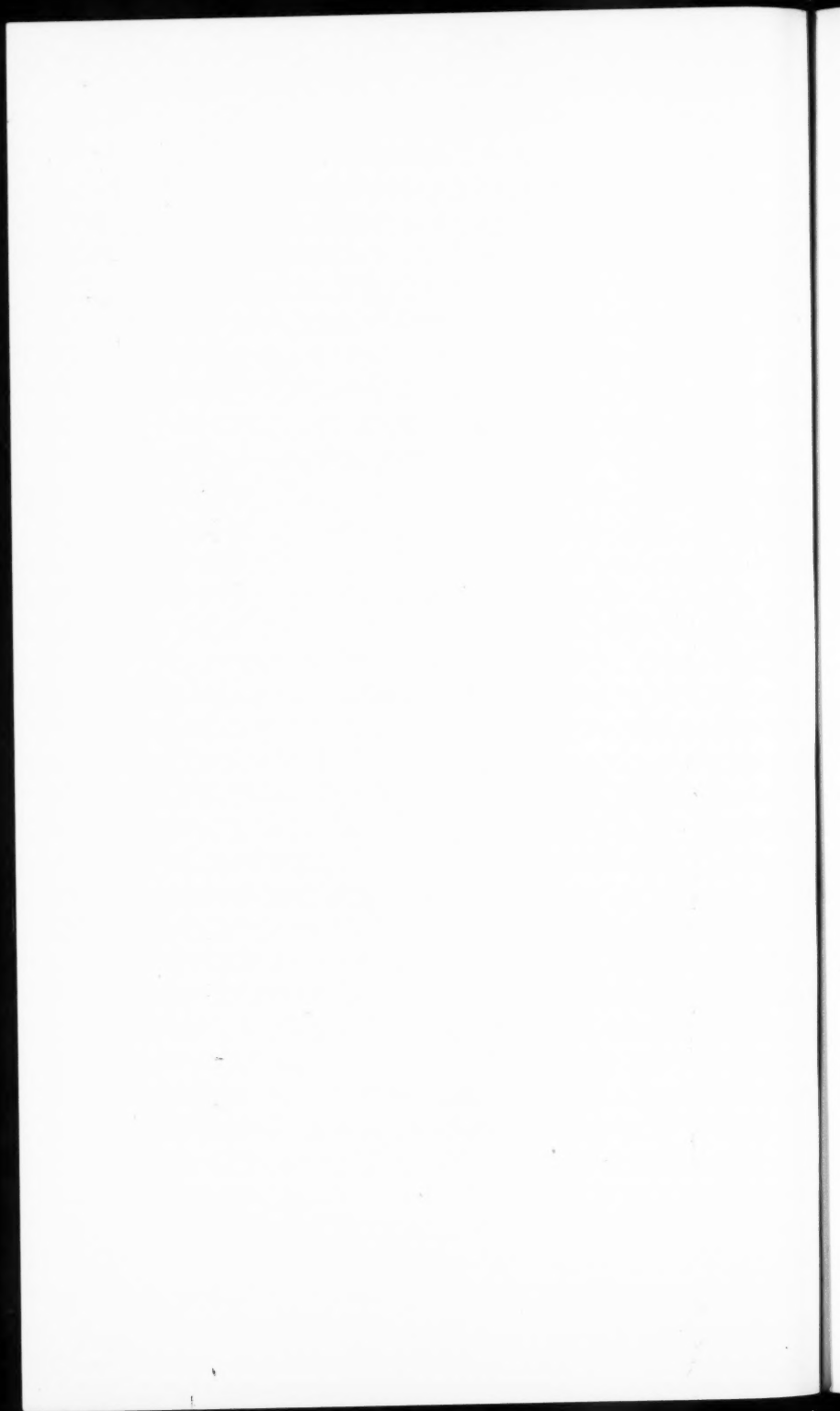
---

THE EFFECT OF PRESSURE ON THE  
ELECTRICAL RESISTANCE OF CERTAIN  
SEMI-CONDUCTORS

By P. W. BRIDGMAN

THE ELECTRIC RESISTANCE TO 30,000 kg/cm<sup>2</sup>  
OF TWENTY NINE METALS AND  
INTERMETALLIC COMPOUNDS

By P. W. BRIDGMAN



# THE EFFECT OF PRESSURE ON THE ELECTRICAL RESISTANCE OF CERTAIN SEMI-CONDUCTORS

By P. W. BRIDGMAN

## CONTENTS

INTRODUCTION.....	127
APPARATUS AND METHOD.....	128
RESULTS.....	131
Zinc Oxide.....	131
Manganese oxide.....	131
Nickel Oxide.....	134
Titanium oxide.....	135
Vanadium Oxide.....	135
Uranium oxide.....	137
Ferric oxide.....	137
NiTiO <sub>3</sub> .....	138
Germanium.....	139
A. n-type germanium.....	139
B. p-type germanium.....	141
Silicon.....	142
A. n-type silicon.....	142
B. p-type silicon.....	143
SUMMARY.....	147

## INTRODUCTION

Recent theoretical successes in accounting for the resistance of semi-conductors, and in particular that of Bardeen<sup>1</sup> in explaining the effect of pressure on the resistance of tellurium, suggest the desirability of determining the effect of pressure on the resistance of other semi-conductors. A few measurements already exist, for example, on tellurium<sup>2</sup> and Ag<sub>2</sub>S.<sup>3</sup> The resistivity of these substances is comparatively low, and the effect of pressure is to decrease greatly the resistance. In the following a number of substances are examined with higher resistances. By the use of a modified technique, the pressure range for these measurements has been increased to 50,000 kg/cm<sup>2</sup>, the previous range of my measurements on tellurium having been 30,000. It has also been possible to extend the temperature of measurement to 200° C. No resistance measurements on material of this class can hope to have the precision of measurements on such materials as the metals, and the present measurements are no exception. Apart from limitations of the method, the material is almost never well defined, and minute impurities or differences in handling may have a large effect on the resistance. The result is that reproducible

results are very difficult to obtain—all that can be hoped for is a qualitative picture of the situation. These difficulties justify one in being satisfied with cruder techniques in measuring resistance than would be tolerated if one were working with metals.

In the following, rough measurements are presented of the resistance of a number of semi-conducting oxides which were supplied by the courtesy of Dr. John Bardeen of the Bell Telephone Laboratories. These were measured up to  $50,000 \text{ kg/cm}^2$  at room temperature,  $100^\circ$  and  $200^\circ \text{ C}$ . In addition, measurements have been made up to  $30,000$  at room temperatures on silicon and germanium of the n- and p-types, also supplied by the Bell Telephone Laboratories. These measurements to  $30,000$  are capable of all the precision previously obtained in the measurement of metals over the same range.

#### APPARATUS AND METHOD

The most important limitation on technique imposed by extending the pressures to  $50,000 \text{ kg/cm}^2$  arises from the difficulty of finding a suitable medium for transmitting pressure to the specimen. At room temperature all substances ordinarily liquid or gaseous freeze, except helium, and the technical difficulties in handling this seem at present prohibitive. Some insulating solid must be used which has a sufficiently low plastic yield point to transmit a tolerable approximation to hydrostatic pressure. To achieve this, not only must a suitable material be found, but the geometrical design must be such as to minimize the tendency to build up stress differences. These geometrical requirements mean that one must operate with the simplest possible design, which in turn means a single electrically insulated lead into the apparatus, which in turn means that measurements must be made with a bridge instead of the potentiometer which was possible formerly when three insulated leads were available.

In my former measurements of shearing under pressure,<sup>4</sup> there is a considerable body of experimental material to facilitate the selection of the best transmitting solid. Among the many substances formerly examined  $\text{Ag}_2\text{SO}_4$  is nearly unique in the low value of the shearing stress required for plastic flow and its approximate independence of pressure. Further preliminary examination showed that its electrical conductivity was negligible in the pressure and temperature range contemplated here.  $\text{Ag}_2\text{SO}_4$  has accordingly been used as the pressure transmitting medium in the following. For this purpose, it is essential that it contain no trace of moisture. In order to remove moisture it was always baked out in vacuum at  $400^\circ \text{ C}$ . immediately before use in the pressure apparatus.



The general arrangement of the pressure vessel with the specimen in place is shown in Figure 1. One of the chief problems of design was to provide for emptying the pressure vessel after completion of a run. This was made possible by the conical closing sleeve *C*. On termination of the run the screw plug and block *B* are removed and the vessel then emptied by pushing out the cone with a ramrod hollowed to receive the insulating stem. The insulation is mica on the flat bearing surfaces and pipe stone on the cylindrical surfaces. The mica should not be more than 0.005 inch thick—otherwise it will cut through. The pressure vessel after charging is mounted in the conventional way in the double hydraulic press which has been formerly used<sup>5</sup> in measurements to 50,000 kg/cm<sup>2</sup>.

The material to be measured, which is originally in the form of powder, is formed in position by compressing with a plunger in an arbor press. It is further consolidated before the regular measurements by an initial application of pressure in place in the press. The electrical resistance was measured between the insulated stem and a ground wire soldered to the press. Any contact resistances in any of the metallic parts of the circuit were entirely negligible. Resistance was measured with a box bridge up to 100,000 ohms. Higher resistances were determined by the galvanometer deflection with a known e.m.f. in series, calibration having been made with a standard megohm.

The temperature bath was of no. 550 silicone fluid, rapidly stirred with three turbine stirrers. Resistance heating was used, manually controlled. Temperature was read with a copper-constantan thermocouple inserted in a deep probe hole in the conical steel sleeve surrounding the pressure vessel. Temperature fluctuation during a run was usually one or two degrees. The maximum pressure of 50,000 kg/cm<sup>2</sup> was applied only at room temperature. At 200° the maximum pressure was restricted to 40,000 kg/cm<sup>2</sup> in order to minimize the danger of fracturing the pressure vessel.

Measured resistances were converted to specific resistance by assuming only radial flow from the central electrode of Figure 1, and a logarithmic variation of potential with the radius. Any end effects and any distortion of the apparatus with pressure were neglected. The dimensions of the apparatus are such as to result in the relation:

Specific resistance = 2.7 measured resistance, or

$$\log_{10} \rho = \log_{10} R + .431$$

The resistance so calculated is doubtless crude, but is probably adequate in view of the other uncertainties. The proportional effects of pressure are usually large and naturally expressed on a logarithmic scale. The major source of uncertainty in the results probably arises

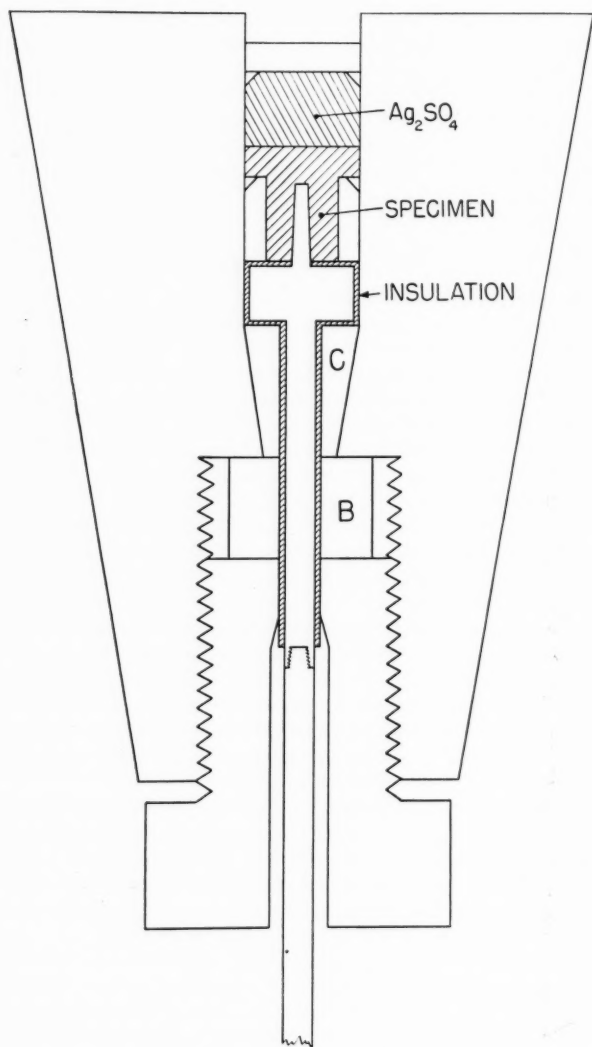


FIGURE 1. Pressure vessel for measurement of resistance of semi-conductors to 50,000 kg/cm<sup>2</sup> and 200 C.

from ill-defined contact resistance between the particles of the originally powdered material. In view of the magnitude of the pressure, however, it would seem that the presumption is that this is not important. The material usually emerged after measurement in a hard and highly compacted condition.

None of the uncertainties inherent in the measurement of the compacted powders in the apparatus for 50,000 kg/cm<sup>2</sup> apply to the measurements on germanium and silicon in the 30,000 apparatus. This material was in the form of massive fused rods and the pressure was truly hydrostatic.

### RESULTS

*Zinc Oxide (ZnO).* This was supplied by the Bell Telephone Laboratories who in turn had obtained it from the New Jersey Zinc Company, "Grade XX101." The resistivity at 25° C. given by the Bell Telephone was  $10^8$ , which is in essential agreement with the results found in the present work. Two fillings of the apparatus and two sets of runs were made with this material. The second set-up was made in order to check the large increase of resistance produced by pressure at 200°, an unusual effect shown by only one other material. The second set-up essentially confirmed the results of the first. The results of the second set-up are shown in Figure 2. It will be seen that the sign of the pressure effect changes consistently with temperature. At room temperature resistance decreases by a factor of the order of ten for a pressure of 50,000 kg/cm<sup>2</sup>, at 100° it is more or less constant, and at 200° increases by the order of ten. The first set-up showed considerably more hysteresis at 100° than did the second. At 200° there was much drift of resistance after every change of pressure, the resistance drifting down, sometimes by a factor of two, to a steady value after five or ten minutes. The drift was in the same direction under both increasing and decreasing pressure; this is inconsistent with the natural explanation as an effect of slow equalization of internal stresses under the frictional effects in the powder. On the first set-up, the initial high resistance was completely recovered on release of pressure and return to room temperature; this point was not checked on the second set-up. In addition to drift, there were polarization effects at 200° on keeping current closed.

*Manganese oxide (Mn<sub>3</sub>O<sub>4</sub>).* This was supplied by the Bell Telephone Laboratories. It had been prepared by heating the carbonate for fifteen hours in the air at 1000° C. The specific resistance at 25° was stated to be  $10^8$ , which agrees with present findings. Immediately before the run it was baked out at 400°. Resistance as a function of pressure and temperature is shown on a logarithmic scale in Figure 3.

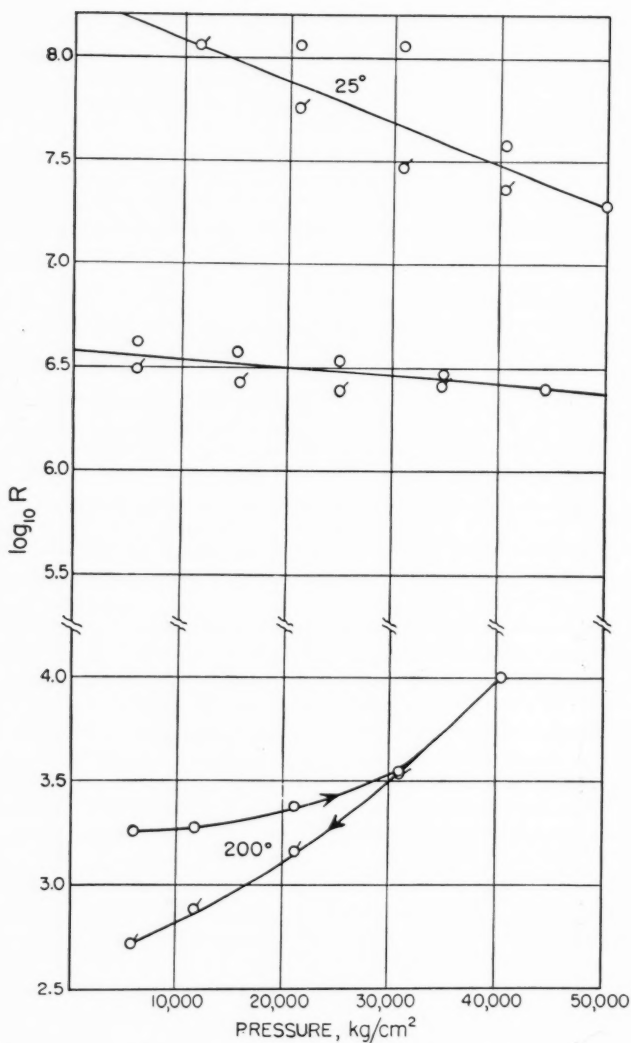


FIGURE 2. The logarithm of the measured resistance of ZnO as a function of pressure and temperature.

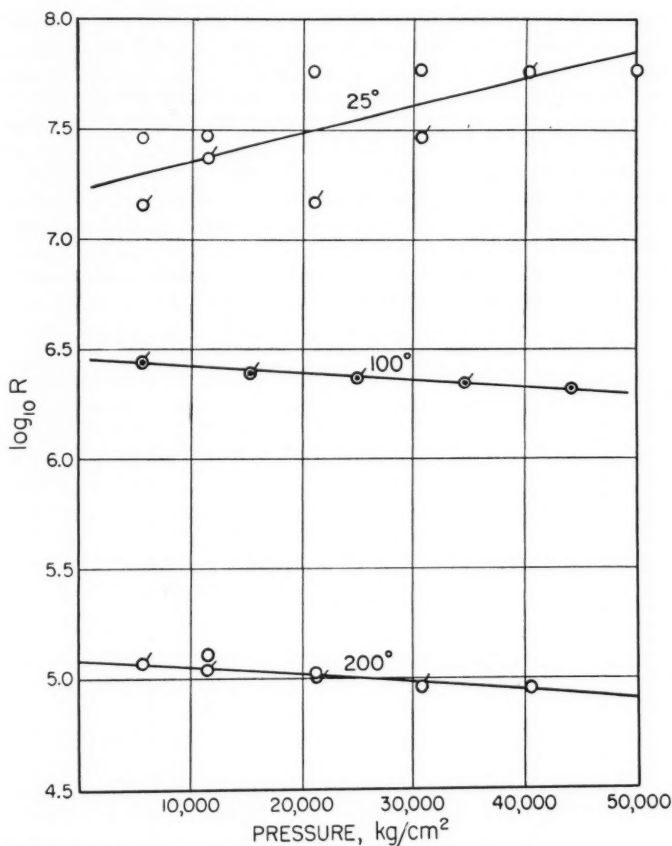


FIGURE 3. The logarithm of the measured resistance of  $\text{Mn}_3\text{O}_4$  as a function of pressure and temperature.

$\text{Mn}_3\text{O}_4$  gave none of the creep effects of  $\text{ZnO}$  but resistance measurements were always clean cut. At the two higher temperatures, resistance is essentially single valued, but at room temperature there is marked hysteresis. It will be noticed that the pressure effects are the exact opposite of those for  $\text{ZnO}$ , for here resistance increases with pressure at the lower temperatures and decreases at the higher. It is true that the effect at the higher temperature appears small in the

diagram, but this is on a logarithmic scale, and the actual readings left no room for uncertainty.

*Nickel oxide (NiO).* This was prepared by the Bell Telephone Laboratories by heating the carbonate to  $1000^{\circ}\text{C}$ . for fifteen hours in the air. The specific resistance stated by them was  $10^8$  to  $10^9$ , but as set up in my apparatus it was much less, close to  $10^5$ . This was checked by emptying the apparatus and refilling four times, in the thought that there might have been an accidental contamination with conducting dirt, but always with the same result. In the endeavor to get a higher resistance the material was baked out again in quartz at  $1000^{\circ}$ . There would seem no doubt that  $10^5$  represents the correct resistance of the material actually used.

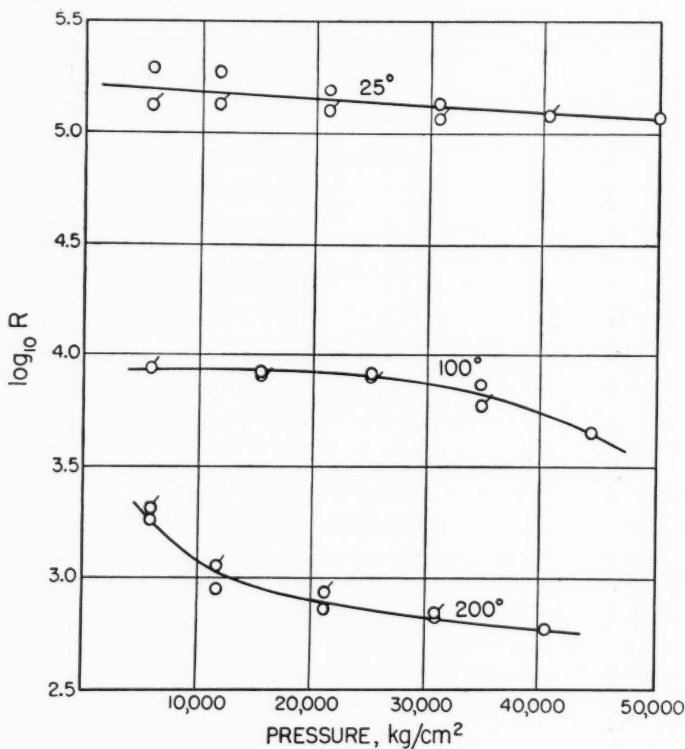


FIGURE 4. The logarithm of the measured resistance of NiO as a function of pressure and temperature.

The experimental results are shown in Figure 4. The measurements were definite, with little hysteresis. Resistance tends to decrease with pressure at all temperatures, the effect becoming greater at the higher temperatures. At 100° and 200° the relation is definitely not linear, and the manner of deviation from linearity is different at the two temperatures.

*Titanium Oxide ( $TiO_2$ ).* This was supplied by the Bell Laboratories who obtained it from the Titanium Pigment Corporation, their "Titanox AMO no. 3552." The specific resistance was stated to be  $10^{12}$  at 25° C., but this is much higher than the value found in the present apparatus, which was only  $10^{8.5}$ .

The experimental results are shown in Figure 5. At 25° and 100° resistance decreases with increasing pressure, but with marked hysteresis. At 200° there are marked seasoning effects, the behavior settling down into a small increase of resistance with pressure. At this temperature there were marked polarization effects on closing the circuit; the readings shown were the steady state readings after initial drift had ceased.

The very large drop of resistance between 100° and 200° would suggest that this substance at 200° is near its intrinsic range. If so, experience with other semi-conductors such as tellurium or silver sulfide would suggest a large decrease of resistance with pressure. On the other hand, the polarization effects would suggest conduction by an electrolytic mechanism, which is consistent with the positive pressure coefficient.

*Vanadium Oxide ( $V_2O_5$ ).* This was prepared by the Bell Laboratories by recrystallization from the melt by cooling slowly from 700° C. to room temperature (from ammonium metavanadate). As received it was in the form of large dark red plates, and the specific resistance was stated to be  $10^4$  to  $10^5$ . For the present experiments it was ground to powder in an agate mortar and baked out at 400° C. My measurements gave consistently, whether the powder was or was not baked out, a lower specific resistance, in the neighborhood of  $10^3$ . Measurements on the massive crystals also gave the same resistance. It is to be considered whether the resistance of this material undergoes a slow change with time, my measurements having been made six months after receiving it.

The experimental results are shown in Figure 6. Resistance drops with increasing pressure at all temperatures, less at the higher temperatures. At 25° there is marked hysteresis, which becomes negligibly small at the higher temperatures. At no temperature was there drift or polarization effects.

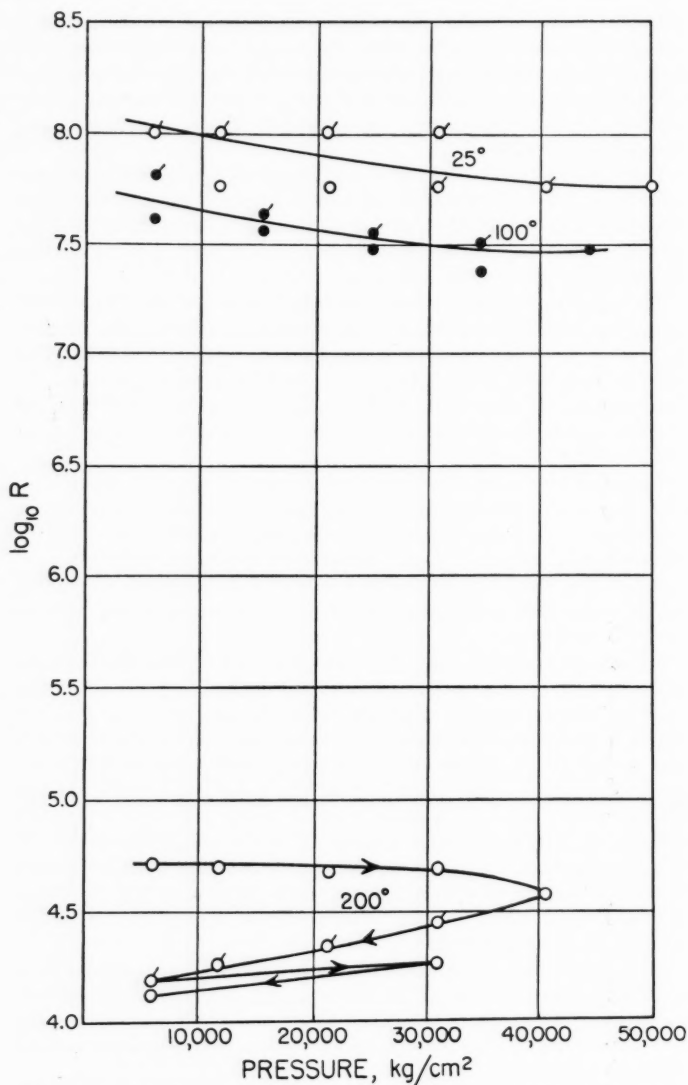


FIGURE 5. The logarithm of the measured resistance of  $\text{TiO}_2$  as a function of pressure and temperature.



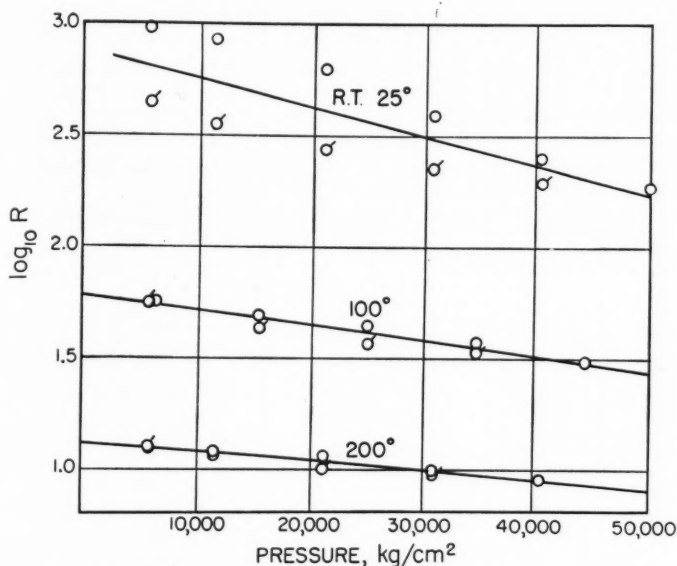


FIGURE 6. The logarithm of the measured resistance of  $\text{V}_2\text{O}_5$  as a function of pressure and temperature.

*Uranium Oxide ( $\text{U}_3\text{O}_8$ ).* This was supplied by the Bell Laboratories who in turn obtained it from Dupont Company. The resistance stated by the Bell Laboratories at 25° C. was  $10^4$ . My value, for the packed powder "as received" was lower by approximately a factor of ten. The resistance proved to be unusually sensitive to the degree of packing.

The experimental results are shown in Figure 7. Resistance decreases at all temperatures with pressure, the coefficient being larger at the lower temperatures. There is also very marked hysteresis which is larger at the lower temperatures. The resistance did not drift after change of pressure nor show polarization effects.

*Ferric Oxide ( $\text{Fe}_2\text{O}_3$ ).* This was prepared by the Bell Telephone Laboratories by heating to 1100° C. for sixteen hours in oxygen. It was provided in the form of a massive bar. For the present measurements the massive material was ground in an agate mortar and baked out at 400°.

Satisfactory results were not obtained for the effect of pressure on this substance. At none of the three temperatures was it possible to

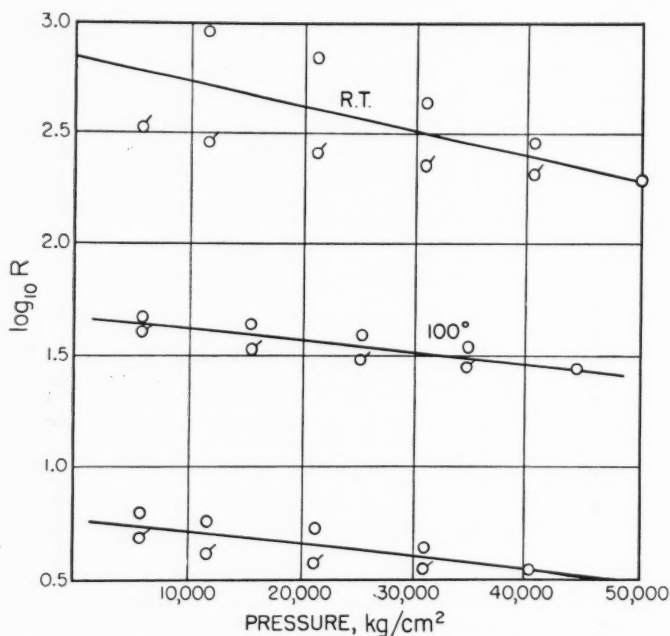


FIGURE 7. The logarithm of the measured resistance of  $U_3O_8$  as a function of pressure and temperature.

establish definitely any effect of pressure at all. At  $25^\circ$  the specific resistance was about half that determined by the Bell Telephone Laboratories, which was  $10^9$ . At  $100^\circ$  the resistance was less by a factor of ten. At  $200^\circ$  the resistance had dropped to something of the order of  $10^5$ , but the readings were very unsatisfactory because of various fluctuations and unsteadinesses and no effect of pressure could be certainly established.

*NiTiO<sub>3</sub>*. This was prepared by the Bell Telephone Laboratories by heating to  $1200^\circ$  C. for twenty hours in oxygen. The resistance was determined by them as  $10^{12}$ .

Again no satisfactory results were obtained under pressure. At the two lower temperatures the resistance was so high as to be beyond the range of the present apparatus. At  $200^\circ$  the resistance appeared to drop with pressure from  $10^9$  to  $10^8$  for the 50,000 kg/cm<sup>2</sup> range. However, this is so much higher than the resistance of any of the other

materials at this temperature that it is not at all certain that it was a legitimate effect but it may have been due to some extraneous factor, such perhaps as conductivity in the  $\text{Ag}_2\text{SO}_4$  transmitting medium.

*Germanium.* The material was supplied by the Bell Telephone Laboratories in both n- and p-types. All specimens were in the form of massive single crystal rods of the general order of 3 cm. long and 3 mm. on a side in square cross section. The measurements were made only at room temperature, in the apparatus for 30,000 kg/cm<sup>2</sup>, with pressure transmitted by a true liquid (pentane). The specimens at first supplied by the Bell Laboratories were provided with four electrodes, as indicated in Figure 8, for measurement by a potentiometer

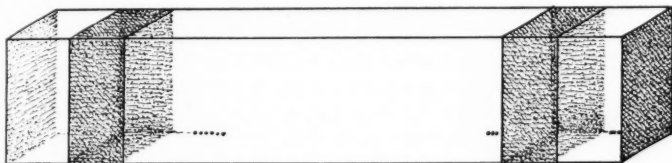


FIGURE 8. General arrangement of potential and current terminals on specimens of germanium and silicon. The current electrodes are copper plated onto the flat ends.

method. It is somewhat of a trick to attach these electrodes. It was done by first electroplating the entire specimen with rhodium, and blasting away the rhodium where not wanted, and copper plating the remaining rhodium. It appeared to me, however, that the use of potential terminals on specimens of these dimensions might be questionable because of the great difference in conductivity between germanium and copper, so that distortion of the lines of current flow by the electrodes was to be anticipated. If this distortion varied with pressure then a false pressure coefficient might be obtained. The first measurements were therefore made by a bridge method with terminals soldered to the current terminals as originally provided and the potentiometer terminals removed with sandpaper.

*A. n-type Germanium.* The first measurements were made on an n-type specimen, with the potential terminals removed as just described. The specific resistance of this at room temperature was 11.3 ohm cm. and its mean temperature coefficient of resistance between 0° and 23° + .00324. The results are shown in Figure 9. It will be noticed that the resistance is single valued in pressure, with no hysteresis, and with a rapidly accelerating rise of resistance at higher pressures. This was in sharp contrast to the results presently ob-

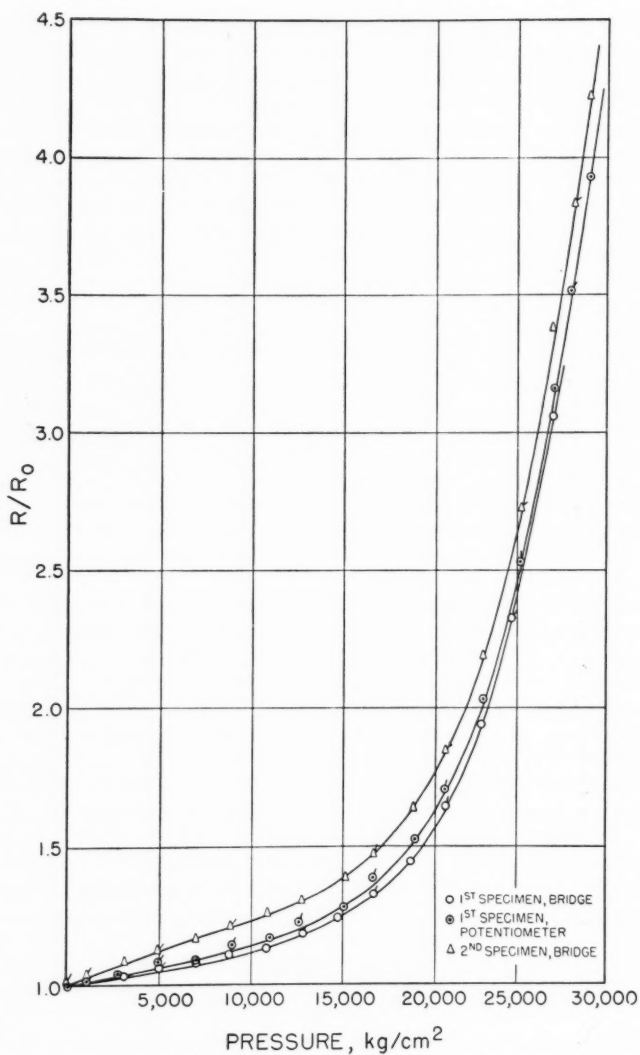


FIGURE 9. The relative resistance of two specimens of n-type germanium at room temperature as a function of pressure.

tained with the p-type, which showed only a comparatively small change. At Dr. Bardeen's suggestion the specimen was therefore returned to the Bell Laboratories to see whether examination might disclose any unusual feature in this particular specimen. Nothing was found. Opportunity was taken to reattach the potential electrodes, it not being certain that some unexpected behavior of the contact resistances might be responsible, and the specimen returned for remeasurement under pressure. The second measurement was made by the potentiometer method, but with essentially the same result, as shown by the second curve in Figure 9. In order to confirm this result, a second specimen of n-type germanium was then measured. This was described as "exceptionally pure" with a specific resistance of 18.5 ohm cm. at room temperature, and mean temperature coefficient of resistance between 0° and 25° of +.00065. Measurements were made on this by the box method with current terminals only and are shown also in Figure 9. It will be seen that the results at the higher pressures are essentially the same as for the other specimen. At the lower pressures the effect of pressure in increasing resistance is of the order of twice as great as for the other specimen. There would seem no reason to question that n-type germanium has an accelerated rise of resistance beginning in the neighborhood of 15,000 kg/cm<sup>2</sup>, and that the relation between pressure and resistance is single valued over the entire pressure range.

*B. p-type Germanium.* Two specimens of this were measured. The first had a specific resistance of 1.6 ohm cm. at room temperature and a mean temperature coefficient of resistance between 0° and 22° of + 0.00815. As provided, this specimen had four terminals, but for measurement the two potential terminals were sandpapered off and measurement made by the box method between electrodes soft soldered to the two terminals plated over the flat ends. The results are shown in Figure 10; this is for the initial application of pressure to the virgin specimen. Resistance decreases with increasing pressure, by a comparatively small amount and approximately linearly, with little permanent effect of the first application of pressure.

The second specimen contained a small amount of gallium as the acceptor impurity (the acceptor impurity was not stated for the first specimen). Its specific resistance at room temperature was 3.35 ohm cm. and its mean temperature coefficient of resistance between 0° and 26° + 0.00825. The resistance was measured by the box method between current terminals, potential terminals never have been attached to this specimen. Total resistance was of the order of 40 ohms. The results are shown also in Figure 10. It will be seen that there is

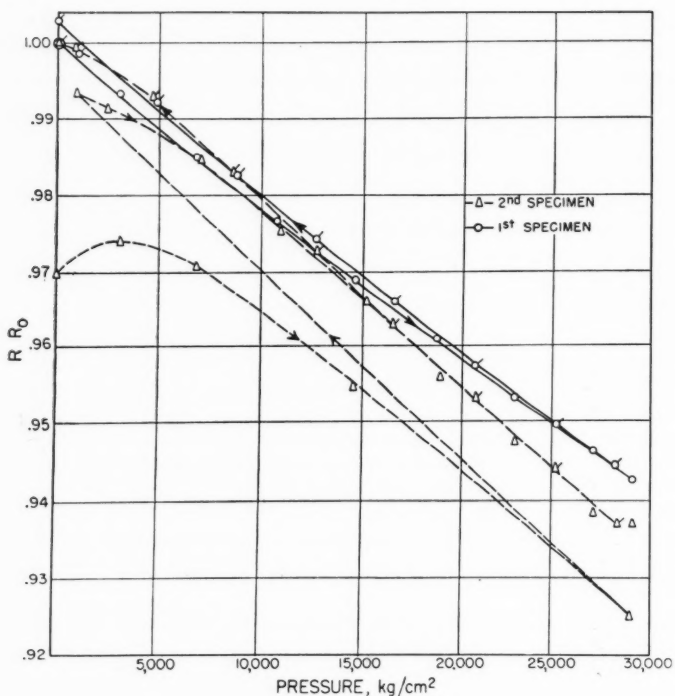


FIGURE 10. The relative resistance of two specimens of p-type germanium at room temperature as a function of pressure.

a considerably larger seasoning effect on the initial application of pressure than for the first sample, but that on the second application it settles down to nearly the same behavior. It would appear, therefore, that a slight nearly linear decrease of resistance under pressure is characteristic of p-type germanium over a range of absolute conductivity of at least two fold.

*Silicon.* A number of runs were made on four different specimens in the apparatus for 30,000 kg/cm<sup>2</sup> at room temperature. The results showed great variability and inconsistencies. A true characterization of the effect of pressures on the resistance of silicon in its various forms will have to wait until more reproducible material is available.

*A. n-type Silicon.* The Bell Laboratories reported difficulty in finding a suitable high resistance specimen. The specimen sent was

said to have a "fairly high" resistivity. The specific resistance of this specimen was 3.9 ohm cm., and the mean temperature coefficient of resistance between 0° and 24° - 0.0236. Measurements were made by the box method with current terminals plated on and soft soldered leads.

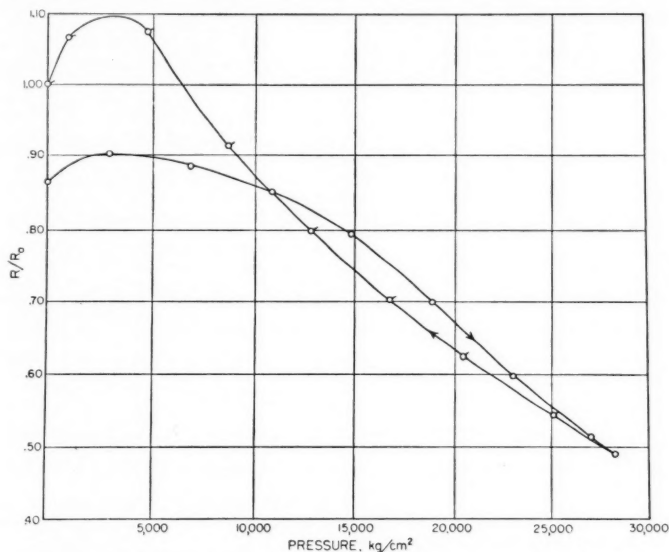


FIGURE 11. The relative resistance of a specimen of n-type silicon at room temperature as a function of pressure.

The effect of the initial application of pressure is shown in Figure 11. The seasoning effects are large. Roughly, the effect of 30,000 kg/cm<sup>2</sup> is to decrease the resistance to about one half its initial value. The sign is thus opposite from that of n-type germanium.

*B. p-type Silicon.* Measurements were made on three specimens. The first two were from the same melt, with a specific resistivity at room temperature of 1.0 ohm cm. and a mean temperature coefficient of resistance between 0° and 24° of +0.00239. The ultimate origin of this was the DuPont Company, and it was described as "high purity silicon." Three runs were made to 30,000 on the first of the two specimens—the first two by the potentiometer method with four electrodes and the third by the box method with the potential electrodes removed by sandpapering. There were appreciable seasoning

effects, but these were not large and the three runs gave essentially consistent results. The result of the third run is shown in Figure 12. Measurements on the second sample were made by the box method with the potential electrodes removed. One run was made to 30,000 kg/cm<sup>2</sup>, the results of which are shown in Figure 13. Qualitatively the character of the results is the same as for the other specimen from the same melt, but the details differ.

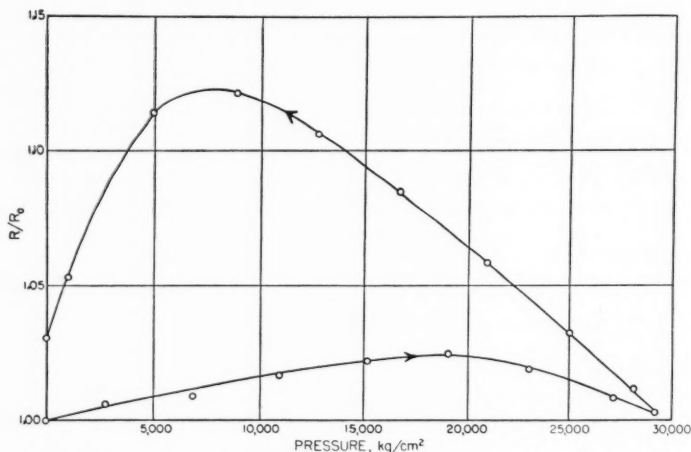


FIGURE 12. The relative resistance of a specimen of p-type silicon at room temperature as a function of pressure.

The third specimen originated in DuPont, and was described as "Hyper pure." Its specific resistance at room temperature was 1.56 ohm cm., and the mean temperature coefficient of resistance between 0° and 25° was  $-.0108$ , of the opposite sign from the specimen from the other melt. Measurements were made by the box method with two electrodes. The result of the first application of pressure to the virgin specimen is shown in Figure 14. There is enormous hysteresis. Unfortunately one of the electrodes was accidentally damaged after the conclusion of the run, so that a second application of pressure could not be made.

In addition to the measurements just described to 30,000 kg/cm<sup>2</sup>, silicon was also measured in the 50,000 apparatus at 25°, 100° and 200°. This material was of unknown type. It was obtained directly through the courtesy of Professor Nix of the University of Pennsyl-



vania but again the ultimate origin was the DuPont Company. It was in the form of single crystal needles, of the order of 1 cm. long and perhaps half a millimeter in diameter. The crystals were iridescent from some sort of surface action. For the measurements the crystals were reduced to powder in an agate mortar and packed into the pressure vessel as already described. As thus mounted, the specific

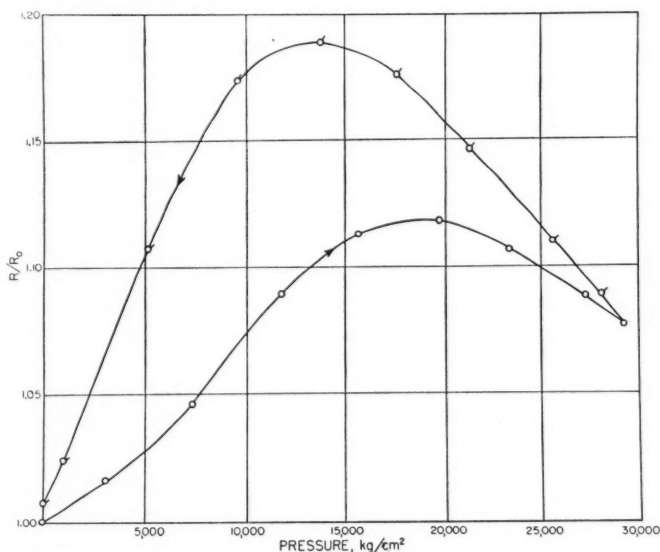


FIGURE 13. The relative resistance of another specimen of p-type silicon from the same melt as that of Figure 12 at room temperature as a function of pressure.

resistance at atmospheric pressure at room temperature was nearly 100. The high value of this compared with the values in the neighborhood of unity already given for the various massive specimens, makes it probable that the resistance was largely contact resistance between the crushed grains. Runs to 50,000 were made as follows: two at 25°; one at 100°; one at 200°; and finally, one at 25° again. There were large seasoning effects on the initial application at room temperature, but in spite of this the final zero was close to the original. At all temperatures resistance drops with increasing pressure, and by approximately the same factor, 4.5, for the 50,000 range. If logarithm

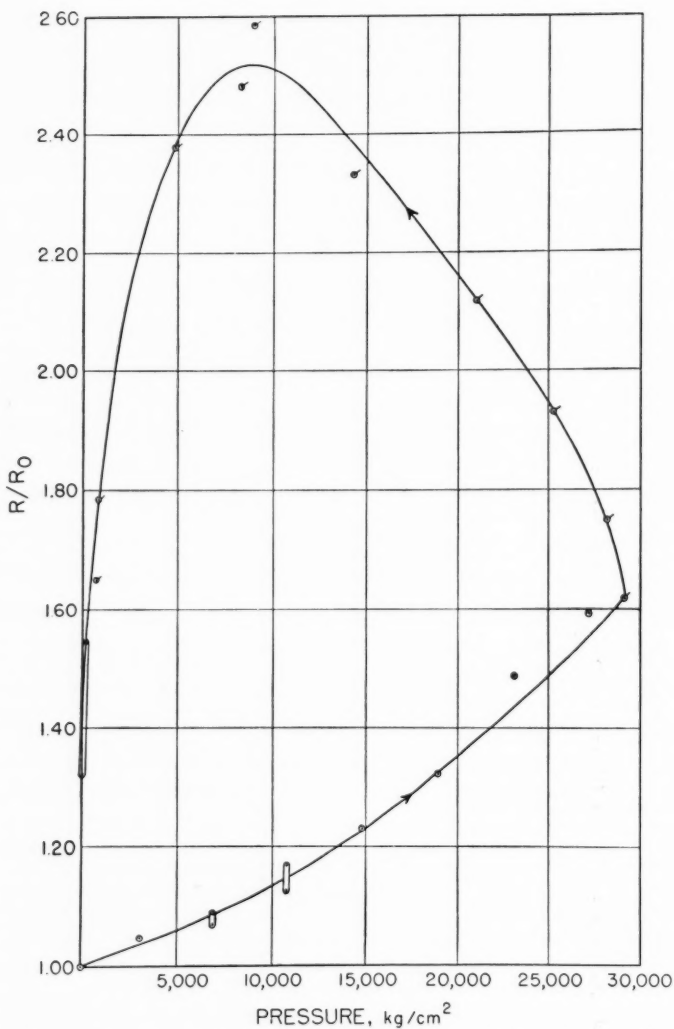


FIGURE 14. The relative resistance of a specimen of silicon from another melt at room temperature as a function of pressure.

of pressure is plotted against pressure a linear relation is obtained for the mean of readings with increasing and decreasing resistance. Superposed on this mean linear relation is a very considerable hysteresis, the width of the loop being half the total pressure effect at 25° and four tenths of it at 100° and 200°. Recovery of zero was close for all applications of pressure except the first.

#### SUMMARY

The electrical resistance of seven oxides has been measured to 50,000 kg/cm<sup>2</sup> at room temperature, 100° and 200° C. The resistance of all these oxides decreases with rising temperature by several powers of ten. There is no common type of behavior under pressure. The effect of pressure is to change the resistance in either direction by amounts running up to a factor of ten or sometimes somewhat more. In all cases except one, Mn<sub>3</sub>O<sub>4</sub>, resistance decreases under pressure at room temperature. Resistance unusually decreases under pressure at 200°; the only exceptions of an increasing resistance are afforded by ZnO and TiO<sub>2</sub>. The proportional change of resistance tends to be less numerically for the higher temperature. All the oxides show marked hysteresis between pressure and resistance, greater at the lower temperatures in general. Part of this hysteresis may be due to failure of pressure to be truly hydrostatic.

The resistance of germanium and silicon was measured under truly hydrostatic conditions to 30,000 kg/cm<sup>2</sup> at room temperature only. Two specimens of n-type germanium, of specific resistances of 11.3 and 18.5 ohm cm. at room temperature, show an increase of resistance by a factor of 4.5 under 30,000 kg/cm<sup>2</sup>, the increase being far from linear, with a very rapid upturn in the neighborhood of 20,000 kg/cm<sup>2</sup>. Two specimens of p-type germanium of specific resistances of 1.6 and 3.35 showed a decrease of resistance under the same pressure of approximately 6 per cent. After initial seasoning effects the relation between pressure and resistance becomes approximately linear. These results for germanium were fairly clean cut and reproducible. Results for silicon were not so clean cut, presumably because the specimens were not so satisfactory. An n-type silicon, with specific resistance of 3.9 ohm cm. at room temperature, showed an approximately linear decrease of resistance to one half the initial value, but with marked hysteresis. Three specimens of p-type silicon of specific resistance from 1.0 to 1.56 ohm cm. showed enormous hysteresis between resistance and pressure, resistance on the whole rising with increasing pressure and there being a very pronounced maximum resistance with decreasing pressure.

It is a pleasure to acknowledge the assistance of Mr. L. H. Abbot, who made the measurements on germanium and silicon, and of Mr. Charles Chase, who set up the experiments on the oxides.

LYMAN LABORATORY OF PHYSICS,  
Harvard University, Cambridge, Mass.

#### REFERENCES

1. J. Bardeen, Phys. Rev. 75, 1777, 1949.
2. P. W. Bridgman, Proc. Amer. Acad. 72, 201, 1938.
3. Fritz Montén, Arkiv for Matematik Astronomi och Fysik, 4, No. 31, 1908.
4. P. W. Bridgman, Proc. Amer. Acad. 71, 387-460, 1937.
5. P. W. Bridgman, Proc. Amer. Acad. 74, 22, 1940.

# THE ELECTRIC RESISTANCE TO 30,000 kg/cm<sup>2</sup> OF TWENTY NINE METALS AND INTERMETALLIC COMPOUNDS

By P. W. BRIDGMAN

## TABLE OF CONTENTS

INTRODUCTION .....	149
DETAILED PRESENTATION OF DATA .....	152
Beryllium .....	152
Magnesium .....	153
Aluminum .....	153
Titanium .....	153
Chromium .....	155
Nickel .....	156
Cobalt .....	159
Zirconium .....	159
Columbium .....	160
Molybdenum .....	160
Rhodium .....	160
Palladium .....	161
Indium .....	161
Lanthanum .....	162
Cerium .....	164
Praseodymium .....	168
Neodymium .....	169
Tantalum .....	169
Tungsten .....	170
Iridium .....	170
Platinum .....	170
CuZn .....	171
AgZn .....	171
AuZn .....	171
Cu <sub>3</sub> Zn <sub>8</sub> .....	172
Ag <sub>5</sub> Zn <sub>8</sub> .....	172
Ag <sub>2</sub> Al .....	174
Sb <sub>2</sub> Tl <sub>7</sub> .....	174
Carboloy .....	175
DISCUSSION AND SUMMARY .....	176

## INTRODUCTION

Thirteen years ago I published data for the effect of pressure up to 30,000 kg/cm<sup>2</sup> on the electrical resistance of nineteen metals.<sup>1</sup> This work was one of the first in the new pressure range, and was done before all the refinements necessary for the maximum precision in that range had been worked out. In particular, the pressure fixed

points had not yet been established by absolute calibration and pressure was measured with the manganin gauge, the constants of which were determined by extrapolation of direct measurements up to 12,000 kg/cm<sup>2</sup> with the assumption that the relation would remain linear over the entire range. It is true that there was pretty good experimental indication, from measurements to 20,000 kg/cm<sup>2</sup>, that any error from this assumption was not likely to be more than a per cent or two.<sup>2</sup> Because of the uncertainty with regard to the pressure the early measurements of resistance were confined to metals for which the effects of pressure were large, which meant that at the same time the deviations from a linear relation between pressure and resistance were large, so that any error from slight deviations from linearity in the pressure scale would not be important.

The necessary refinements in the measurement of pressure have now been worked out so that the slight deviations from linearity in the manganin gauge can be determined for any particular manganin coil by reference to two pressure fixed points,<sup>3</sup> and it is therefore indicated that the resistance measurements should be extended to 30,000 kg/cm<sup>2</sup> for other metals which show a smaller effect of pressure and a closer approach to linearity. In the following, data are presented for all the presently available metals which satisfy this description. The material of the measurements in many cases is the identical specimen which was formerly measured<sup>4</sup> in the range to 12,000 kg/cm<sup>2</sup>, and in fact all the former material has now been remeasured over the wider range except in those instances where material purer than that formerly used is now available. In the cases where the identical material was not used, an indication of the probable purity of the present material has been attempted by measuring the temperature coefficient of resistance at atmospheric pressure. The present measurements were made at room temperature instead of over the temperature range between 0° and 100° as formerly to 12,000. It would, of course, have been preferable if the new measurements had been as complete with respect to temperature as the former ones. However, the present apparatus was not easily adapted to temperature variation, and the previous measurements had shown that any changes in the temperature coefficient of resistance brought about by pressure are minor.

In addition to their interest in themselves, these measurements on resistance are of interest because the compressibility of these same materials is now available<sup>5</sup> for use in any theoretical discussion which may be made of these results. Furthermore, a program of extension of the resistance measurements to 100,000 kg/cm<sup>2</sup> is now well under

way, and as accurate knowledge as possible of the behavior in the lower range of pressure is going to be necessary in determining some of the constants in the unavoidable correction terms at high pressures.

The apparatus was essentially the same as that used thirteen years ago, except for improvements in the technique, especially in the construction of the insulating plug, which now permits so many applications of pressure without renewal that it has ceased to be a source of major annoyance. The apparatus was not thermostated, but allowed to follow the temperature of the room. The experiments were made in two or three hours; in this time the temperature of the massive steel cylinders drifted usually only two or three tenths of a degree, which resulted in a displacement of the zero on completion of the run of only a small fraction of the total effect of pressure. Correction was applied for temperature drift during the run by assuming a linear connection in time between the initial and the final zeroes. Usually 16 readings were made equispaced with respect to pressure, with increasing and decreasing pressure.

The results are presented in terms of  $-\frac{1}{p} \frac{\Delta R}{R_0}$ . The reason for this is that probably the chief interest in extending the measurements over a wide pressure range is to find how the change of resistance departs from proportionality to the pressure and the departure of  $-\frac{1}{p} \frac{\Delta R}{R_0}$  from constancy indicates at once the failure of  $\frac{\Delta R}{R_0}$  to be proportional to pressure. The method of computation was to calculate  $-\frac{1}{p} \frac{\Delta R}{R_0}$  for every observation and to plot this against pressure. Smooth curves were drawn through the experimental points thus plotted, and the results read off at pressure intervals of 5,000 kg/cm<sup>2</sup> and tabulated. In many cases the relation between  $-\frac{1}{p} \frac{\Delta R}{R_0}$  and pressure was sensibly linear. This means that  $\frac{\Delta R}{R}$  may be represented by a second degree expression in the pressure.

Figure 1 shows a sample set of experimental points—for aluminum. The points in the neighborhood of the origin were not always as smooth as for aluminum, particularly if the material was one with a small change of resistance under pressure. The reason is obviously that the percentage accuracy is less at the lower end of the range where the effects are smaller. Also at the lower end of the curve any creep

effects have their maximum. The results presented in the tables are in most cases the mean of the results with increasing and decreasing pressure. It may be that in some cases the creep effects are legitimate and that by averaging in this way something essential was discarded. If so, any such effect was very small and may be disregarded for any

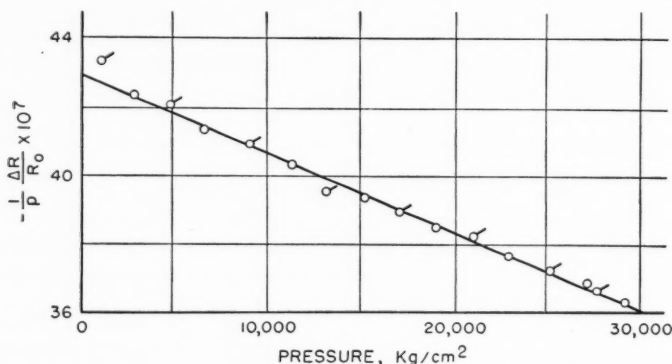


FIGURE 1. The experimental results for aluminum. The plain circles give the readings with increasing pressure: the circles with wings the readings with decreasing pressure.

first approximation. It would have demanded a much more elaborate investigation that I was prepared to undertake to get any physically significant information about such creep effects. One metal, lanthanum, although not exhibiting creep of the zero, did exhibit hysteresis in amount so large that it seemed probable that there was some connection with intrinsic properties of the metal. For this substance the results with increasing and decreasing pressure are reproduced in detail.

The results for several of the metals show cusps in the resistance-pressure relation. These effects are certainly real and connect with similar effects already found for compressibility. For these substances the detailed results will be given. All the other substances will be collected together into a single table, arranged by atomic weight for the elements, with the intermetallic compounds last. In the detailed presentation of data any special features of the individual substances will be mentioned in detail.

#### DETAILED PRESENTATION OF DATA

*Beryllium.* The specimen was a rod 0.102 cm. in diameter and 3.8 cm. long turned down from a rod 1.25 cm. in diameter which was ob-



tained a number of years ago from Professor Chipman of M. I. T. who was making a systematic investigation of its metallographical properties. The small rod was somewhat warped by the turning, indicating some internal strains. It was heated for several hours to 400° C. after turning in order to anneal it, but with problematical effect. It was not possible to either soft or hard solder this metal, and the four terminals for the potentiometer measurements were spring clips. The mean temperature coefficient of resistance between 0° and 24° C. at atmospheric pressure was 0.00564, indicating a fairly high probable purity.

The curve of  $-\frac{1}{p} \frac{\Delta R}{R_0}$  against pressure is slightly convex toward the pressure axis. A third degree expression in the pressure would certainly reproduce the results within experimental error.

*Magnesium.* The material was a single crystal of unknown orientation, one made many years ago from stock of known high purity from the Aluminum Co. of America and used previously in measurements of resistance and elastic constants.<sup>6</sup> For the present measurements it was turned in the jewelers lathe in steps of 0.001 inch to avoid disturbing the crystal lattice from an initial diameter of 0.100 inch to 0.070 inch. The terminals were spring clips of silvered piano wire.

The specific resistance at 24.5° was  $4.84 \times 10^{-6}$ . The effect of pressure on resistance is given in Table I.  $-\frac{1}{p} \frac{\Delta R}{R_0}$  against pressure is somewhat convex toward the pressure axis. A third degree expression in the pressure will not reproduce the results within experimental error.

*Aluminum.* This was from the same spool as used previously in measurements of resistance under pressure to low temperatures.<sup>7</sup> The purity was fairly high as indicated by the temperature coefficient at atmospheric pressure. The four terminals for the present measurements were attached with a commercial aluminum solder known by the trade name of "eutectic No. 19."

The effect of pressure on resistance is given in Table I. Within the limits of error  $-\frac{1}{p} \frac{\Delta R}{R_0}$  is linear with pressure over the entire range and the drop is greater than usual, from 0.0429 at atmospheric pressure to 0.0360 at 30,000 kg/cm<sup>2</sup>. This means a second degree relation, and a minimum resistance, judging by an extrapolation, at 104,000 kg/cm<sup>2</sup>, which is far enough away for many things to happen.

*Titanium.* This material has only recently become available in ductile form as a result of the researches of the Dupont Co. The

TABLE I  
 $\frac{1}{p} \frac{\Delta R}{R_0}$  FOR NORMAL METALS

Pres- sure kg/cm <sup>2</sup>	Beryl- lum at 24° 5	Magnesium at 24° 5	Alumi- num at 27° 7	Titanium at 23° 2	Cobalt at 23° 5	Zirconium at 25° 5	Colum- bium at 24° 0	Molyb- denum at 26° 5	Rho- dium at 25° 6	Palla- dium at 26° 1	Indium at 23° 0	Presse- dium at 24° 0
0	0.00000	0.00000	0.00000	0.00000	0.000000	0.000000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000
5,000	1774	540	429	1190	956	3896	1400	1312	1654	2100	1254	1363
10,000	1696	499	417	1150	930	3621	1383	1300	1638	2071	1168	1276
15,000	1630	467	406	1118	904	3346	1366	1289	1622	2042	1089	1200
20,000	1580	440	394	1086	878	3070	1348	1277	1607	2013	1014	1142
25,000	1537	419	383	1063	852	2795	1331	1266	1591	1984	0950	1096
30,000	1494	398	371	1040	826	2520	1314	1254	1575	1955	0896	1054
	1459	381	360	1017	799	2244	1296	1243	1560	1926	0847	1017

Pres- sure kg/cm <sup>2</sup>	Neodym- ium at 23° 6	Tanta- lum at 28° 3	Tung- sten at 28° 4	Iridium at 22° 7	Plati- num at 22° 4	CuZn at 23° 4	AgZn at 24° 0	AuZn at 23° 7	AgZn <sub>2</sub> at 24° 3	AgAl at 26° 0	Sb <sub>2</sub> Th at 26° 4	Car- bonyl at 23° 8
0	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.000000	-0.000000	0.00000	0.00000
5,000	1567	1620	1333	1390	1924	2194	413	3436	470	050	958	246
10,000	1426	1622	1319	1379	1900	2100	393	3354	426	069	872	159
15,000	1318	1621	1305	1368	1879	2042	3734	3272	382	088	830	144
20,000	1228	1614	1291	1358	1858	1995	3569	3189	338	107	780	136
25,000	1151	1598	1277	1347	1832	1852	3394	3107	294	129	740	130
30,000	1087	1580	1263	1336	1807	1815	3252	3025	250	145	701	128
	1031	1550	1248	1326	1780	1870	3124	2942	205	163	673	125

specimen for these measurements was a wire approximately 0.03 inch in diameter, which I owe to the courtesy of the Remington Arms Co., who are licensed by Dupont to produce it. As received it was rather brittle and could not be bent to a right angle of 1/8 inch radius without fracture. An attempt was made to anneal it by heating to a bright red sealed in vacuum into quartz, but with little success. The terminals were nickel, spot welded. At atmospheric pressure the average temperature coefficient of resistance between 0° and 22° was 0.00274. The specific resistance at room temperature was 0.0000772.

It was seasoned before the final measurements by a preliminary application of 30,000 kg/cm<sup>2</sup> with very little permanent change of resistance. The permanent change of zero after the final pressure run was only 0.5 per cent of the maximum pressure effect. In spite of the good stability of the zero, the pressure readings showed unusually large hysteresis of resistance in the normal direction,  $-\Delta R/R_0$  with increasing pressure being 0.01658 and with decreasing pressure 0.01600 at 15,000 kg/cm<sup>2</sup>, the mid point, where the hysteresis was greatest. The results shown in the table are the mean of increasing and decreasing pressure.  $-\frac{1}{p} \frac{\Delta R}{R_0}$  is convex toward the pressure axis, as is normal,

with slight curvature. A third degree expression in pressure would reproduce  $\Delta R/R_0$  within experimental error. When purer material is available the measurements should be repeated.

*Chromium.* This was highly purified electrolytic material prepared at the National Bureau of Standards, which I owe to their courtesy. It was prepared by G. E. Renfro at the Bureau in the form of a tube 300 mm. long, 9 mm. o.d. and 8 mm. i.d. by electrolytic deposition. It was the identical tube for which measurements of thermal expansion have been published in Jour. of Research, N. B. S. 26, 81, 1941. The chemical composition was stated to be Cr 99.3, Fe 0.002, Si 0.002, Mn, Pb, Cu, n.d.

It is known that the resistance of pure chromium shows anomalous effects. Measurements I made a number of years ago on a swaged wire of pure chromium<sup>8</sup> showed a minimum of resistance at atmospheric pressure in the neighborhood of 10° C., the total change of resistance between 0° and 20° being sensibly zero.

For the present measurements a slender rod of trapezoidal section was cut by grinding with a thin wheel from the electrolytic cylinder. Assuming 7.103 for the density, which is the figure given by the Bureau of Standards for the final density after the last thermal expansion excursion, the specific resistance at room temperature was  $19.2 \times 10^{-6}$ . The terminals were spring clips of silvered piano wire.

The resistance at atmospheric pressure showed no trace of the anomaly previously found. Between  $0^\circ$  and  $20^\circ$  resistance increases smoothly and nearly linearly with temperature, with a mean coefficient of 0.00274 (by chance the same as for titanium). The only trace of anomaly in the behavior of resistance with respect to temperature in this range is a slight concavity of the curve of resistance toward the temperature axis, the usual curvature being convex.

There was, however, a very definite anomaly in the pressure behavior, there being a cusp in the curve of resistance versus pressure at 3,400 kg/cm<sup>2</sup> where the slope abruptly decreases. Below this pressure the resistance decreases at an accelerated rate with increasing pressure.

Figure 2, in which the experimental points for  $-\frac{1}{p} \frac{\Delta R}{R_0}$  are plotted against pressure in the lower end of the range up to 5,000 shows on a magnified scale the nature of the anomaly. Above 3,400  $-\frac{1}{p} \frac{\Delta R}{R_0}$  drops off with increasing pressure as is normal, but with exceptionally high curvature. The experimental points all lie smoothly on a single curve within experimental error, with no trace of hysteresis. In Table II,  $-\frac{1}{p} \frac{\Delta R}{R_0}$  is given at intervals of 1,000 kg/cm<sup>2</sup> up to the cusp at 3,400 and beyond that at the customary pressure interval of 5,000 kg/cm<sup>2</sup>, which is close enough.

In spite of the abnormally large curvature shown in Figure 2 graphical extrapolation does not suggest the proximity of a minimum in the resistance.

*Nickel.* This was the identical specimen that I had previously used in measuring the effect of pressure on resistance at low temperatures.<sup>9</sup> It was originally a product of the Research Laboratory of the Leeds and Northrup Company, who had specially prepared it for a high temperature coefficient; this demands exceptional purity. There is obviously something unusual about nickel. My previous measurements at low temperatures showed creep and hysteresis effects which could never be made to vanish, and recent measurements on the compressibility of a single crystal of high purity have shown a cusp in the compressibility curve at 10,000 kg/cm<sup>2</sup> at room temperature.

The temperature coefficient of this sample, determined by special measurements after the present pressure runs, was 0.00573, average between  $0^\circ$  and  $22^\circ$  C.

Consistently with these other indications the resistance as a function of pressure is also anomalous. In Figure 3 are plotted the experimen-

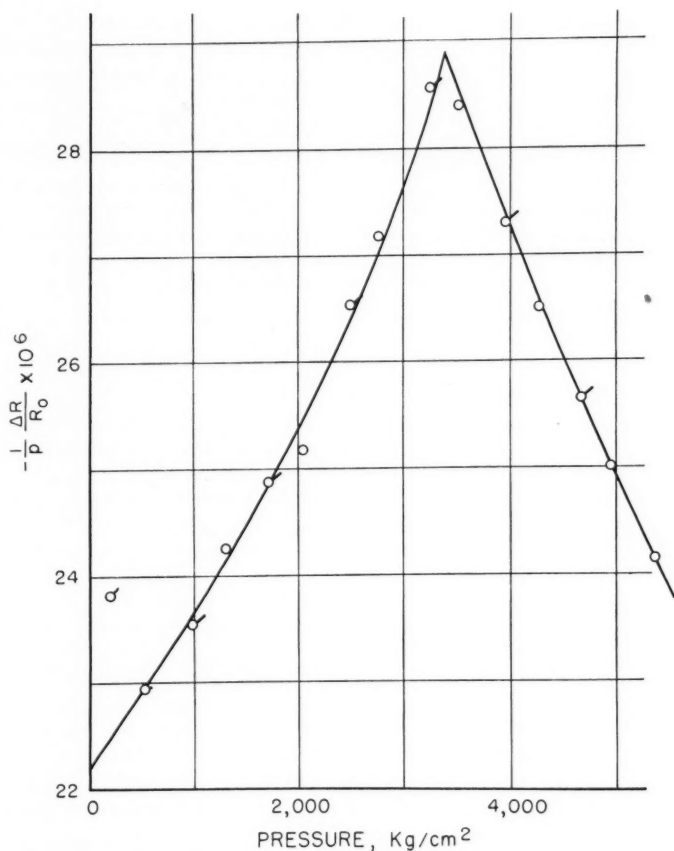


FIGURE 2. The experimental results for chromium at the low pressure end of the range. The circles with wings indicate the measurements with decreasing pressure.

tal values of  $-\frac{1}{p} \frac{\Delta R}{R_0}$  as a function of pressure. It will be seen that there is a sharp change in direction near 10,000  $\text{kg/cm}^2$ , the pressure of the anomaly in compressibility. There is also consistent hysteresis greater than experimental error. The results given in Table III for  $-\frac{1}{p} \frac{\Delta R}{R_0}$  are average results for increasing and decreasing pressure.

TABLE II  
CHROMIUM AT 25°.2

Pressure kg/cm <sup>2</sup>	$-\frac{1}{p} \frac{\Delta R}{R_0}$	Pressure kg/cm <sup>2</sup>	$-\frac{1}{p} \frac{\Delta R}{R_0}$
0	0.0000	5,000	239
1,000	222	10,000	1733
2,000	234	15,000	1380
3,000	251	20,000	1128
3,400	276	25,000	1012
(cusp)	287	30,000	0896

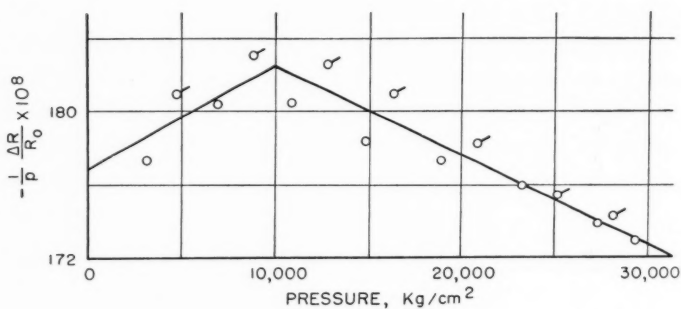


FIGURE 3. The experimental results for nickel. The circles with wings indicate the measurements with decreasing pressure.

TABLE III  
NICKEL AT 24°.7

Pressure kg/cm <sup>2</sup>	$-\frac{1}{p} \frac{\Delta R}{R_0}$	Pressure kg/cm <sup>2</sup>	$-\frac{1}{p} \frac{\Delta R}{R_0}$
0	0.00000	15,000	1800
5,000	1769	20,000	1776
10,000	1800	25,000	1752
(cusp)	1824	30,000	1728

Within error these results can be represented by two linear ranges, one from 0 to 10,000 and the other from 10,000 to 30,000.

*Cobalt.* This was the same specimen that had been used in 1928<sup>10</sup> as the end member of the series in determining the effect of pressure on the resistance of a series of iron-cobalt alloys. It was prepared electrolytically by Mr. W. C. Ellis at Rensselaer Polytechnic Institute under the direction of Dr. M. A. Hunter in connection with his thesis on the properties of the alloys. The mean temperature coefficient of resistance at atmospheric pressure between 0° and 100° as determined by Ellis was 0.00604. Ellis's specific resistance at 20° was  $6.24 \times 10^{-6}$ . Both of these figures are evidence of high purity.

The pressure measurements showed no unusual features. Within experimental error  $-\frac{1}{p} \frac{\Delta R}{R_0}$  is linear in the pressure, with the customary deviations in both directions at the low pressures (below 5,000 kg/cm<sup>2</sup>) where the experimental accuracy is less. The pressure coefficient of resistance extrapolated to atmospheric pressure is  $-0.06956$ , which is practically identical with the result of the 1928 measurements in the range to 12,000, which was 0.06958. The former second degree term in the pressure ( $\Delta R/R_0 = -ap + bp^2$ ) of the former work differs greatly from the present, the former value of  $b$  having been  $0.68 \times 10^{11}$  against  $3.19 \times 10^{11}$  found now. The present value is doubtless to be preferred, both because the wider pressure range by itself gives greater accuracy and because in the present work the deviations from linearity of the manganin gauge were directly determined whereas in the former work the manganin gauge was assumed to be linear.

*Zirconium.* This was the same specimen that had been used in 1928<sup>11</sup> for measurements of the effect of pressure to 12,000 kg/cm<sup>2</sup> on the resistance. It was obtained through the kindness of Dr. G. Holst from the Philips Lamp Works in Eindhoven, Netherlands. Its specific resistance was  $49.2 \times 10^{-6}$ , and the mean temperature coefficient of resistance at atmospheric pressure between 0° and 100°, calculated by linear extrapolation of measurements at 30° and 75°, was 0.00403.

The relation between pressure and  $-\frac{1}{p} \frac{\Delta R}{R_0}$  is linear with an unusually large drop with pressure, indicating unusually high curvature in the relation between pressure and resistance. Extrapolation indicates a minimum of resistance at only 35,300 kg/cm<sup>2</sup>. Expressed in terms of pressure the present measurements give up to 30,000  $\Delta R/R_0 = -3.90 \times 10^{-7}p + 5.5 \times 10^{-12}p^2$  at 25°, the temperature of measure-

ment, against the former results to 12,000 at the same temperature and on the same specimen  $\Delta R/R_0 = -4.12 \times 10^{-7}p + 6.6 \times 10^{-12}p^2$ . On a percentage basis the agreement is not as good as it often is, but it must be considered that there is some compensation between the two coefficients because of their opposite sign and also that the absolute magnitude of the effect is unusually small and there may have been some slight change in the material itself during the 22 years between the two sets of measurement.

*Columbium.* This was obtained in 1946 from the Fansteel Co., the purest which they could supply at that time. The specimen was in the form of a slender rod 1.6 mm. in diameter and 7.1 cm. long. The terminals were spring clips of piano wire. The temperature coefficient of resistance at atmospheric pressure between  $0^\circ$  and  $24^\circ$  was 0.00305, not evidence of specially high purity.

Before the regular pressure run it was seasoned by an initial application of 30,000 with no measurable permanent change of zero. The relation between pressure and  $-\frac{1}{p} \frac{\Delta R}{R_0}$  is sensibly linear, with perhaps more irregularity than usual at the two lowest pressures. The drop of  $-\frac{1}{p} \frac{\Delta R}{R_0}$  with pressure is small, so that any eventual minimum is too far away for extrapolation.

*Molybdenum.* This specimen was used previously in 1932<sup>12</sup> in measurements to liquid oxygen temperatures. It was obtained from the General Electric Co. The temperature coefficient of resistance at atmospheric pressure was 0.00461.

In the range to 30,000 kg/cm<sup>2</sup>,  $-\frac{1}{p} \frac{\Delta R}{R_0}$  is linear within experimental error with very little drop, that is, unusually little curvature in the relation between  $\frac{\Delta R}{R_0}$  and pressure.

*Rhodium.* This was the same specimen that was used in 1932<sup>13</sup> for the determination of the change of resistance under pressure up to 7,000 kg/cm<sup>2</sup> at liquid oxygen temperature. It was obtained from Baker and Co., and judging by the behavior of the resistance below  $0^\circ$  was of somewhat greater purity than a specimen used by Holborn at the Reichsanstalt. Formerly the leads were of platinum welded on; for this work these leads were replaced with copper soft soldered.

A preliminary application of 30,000 was made before the regular readings, but in spite of this the internal accommodation of the material was not as perfect as usual and there was a consistent difference between the readings with increasing and decreasing pressure in the



direction of a normal hysteresis. The fractional decrease of resistance at 15,000 kg/cm<sup>2</sup> with increasing pressure was 0.0240 and with decreasing pressure 0.0244. The mean of increasing and decreasing pressure gives a  $-\frac{1}{p} \frac{\Delta R}{R_0}$  which is linear in the pressure within experimental error and with too small a drop with pressure to invite extrapolation for a possible minimum. Exact comparison with the former results is not possible because of the difference of temperature range and the fact that variation of the pressure coefficient is not linear over such wide intervals of temperature, but there is at least nothing in the former data to indicate any gross inconsistency with the new results.

*Palladium.* This was from the same spool but was not the identical specimen used in 1932<sup>14</sup> for measurement of resistance under pressure at liquid oxygen temperature. It was originally obtained from Baker and Co., their purest. Immediately before present use it was degassed in vacuum at 900°. The specimen was 3.3 cm. long and 1.7 mm. in diameter. The dimensions were such that the resistance was materially higher than usual, permitting measurements of resistance of unusual precision.

Within notably better than the usual precision  $-\frac{1}{p} \frac{\Delta R}{R_0}$  is linear with pressure to 30,000 kg/cm<sup>2</sup>. The rate of decrease is small and any extrapolation for a minimum would be unjustified.

Formerly, measurements were made in the range to 12,000 kg/cm<sup>2</sup> at both 0° and 95° as well as at temperatures below 0°, so that comparison can be made with the present results. Reduced to 26°, the temperature of the present measurements, the former results in the 12,000 range were  $\frac{\Delta R}{R_0} = -2.15 \times 10^{-6}p + 5.4 \times 10^{-12}p^2$  against the present

result in the 30,000 range  $\frac{\Delta R}{R} = -2.10 \times 10^{-6}p + 5.8 \times 10^{-12}p^2$ .

*Indium.* None of the former exceptionally pure material,<sup>15</sup> which had been prepared by T. W. Richards for atomic weight determinations, was any longer available, and I had to use some miscellaneous stock originally obtained from MacKay which had in the meantime been used in the formation of capsules for compressibility measurements to 50,000 kg/cm<sup>2</sup>. The present specimen was extruded to 3 mm. in diameter and 7.5 cm. long. The terminals were of fine tinned copper wire, threaded through holes pierced with a needle through the indium wire, and attached by judicious soft soldering. The average temperature coefficient at atmospheric pressure between 0° and 24°

was 0.00371 against the value 0.00401 over the same temperature range for the former exceptionally pure material.

In spite of the mechanical softness of this metal the pressure measurements were unusually good, with no perceptible difference between increasing and decreasing pressure. The plot of  $-\frac{1}{p} \frac{\Delta R}{R_0}$  against pressure is slightly convex toward the pressure axis. A third degree expression in pressure would represent the results within experimental error.

The initial pressure coefficient of resistance at  $23^\circ$ , the temperature of the present measurements, of the former measurements was  $-1.50 \times 10^{-4}$  against the present value  $-1.25 \times 10^{-4}$ . The discrepancy is in the direction usually associated with impurity.

Any eventual minimum of resistance of the present material is too far away for extrapolation.

*Lanthanum.* The material was freshly obtained from Mackay in massive form. It was extruded into wire 0.96 mm. in diameter from a steel die at a dull red heat, the wire issuing immediately into cold nujol. The mean temperature coefficient of resistance at atmospheric pressure between  $0^\circ$  and  $25^\circ$  was 0.00208 and the specific resistance at  $0^\circ$   $6.13 \times 10^{-6}$ . These figures are to be compared with 0.00213 and  $5.76 \times 10^{-6}$  respectively for a specimen measured in 1927.<sup>16</sup> This latter specimen was obtained from Dr. H. C. Kremers, who stated that it was free from other metals. Judging by the figures above the present sample was not as pure as the former but the difference is not large.

The behavior of resistance in the pressure range to 30,000 was anomalous, there being large hysteresis in the normal direction between the resistance with increasing and decreasing pressure. Furthermore, the direction of curvature is anomalous. With increasing pressure at the low pressure end of the range up to about 15,000 the curvature is normal, that is, resistance decreases at a decreasing rate as pressure increases, but at 15,000 there is reversal, and from here on the decrease of resistance accelerates with increasing pressure. With decreasing pressure the curvature is in the normal direction over the entire extent of the curve. In the search for any discontinuities which might throw light on the abnormal behavior, many more readings were made than usual, 38 against the usual 16. No discontinuities of any sort were found, but on the contrary the readings with both increasing and decreasing pressure lay smoothly on the corresponding branch of the hysteresis loop with deviations of not more than the sensitiveness of the readings, which amounted to one part in

1000 of the pressure effect at the top pressure. Furthermore there was no perceptible creep with time after a change of pressure, something which might have been anticipated if the hysteresis is due to a shifting internal equilibrium.

One might be inclined to ascribe the anomalies to the presumed impurity if it were not that cerium, the next element in the periodic table, shows very large anomalies in specimens known to be of high purity.

The specimen measured in 1927 to 12,000 was sensibly linear with a pressure coefficient at  $25^\circ$ , the temperature of the present measurements, of  $-1.14 \times 10^{-6}$ . This is to be compared with the initial value  $-2.00 \times 10^{-6}$  for the present specimen as given in Table IV.

TABLE IV  
LANTHANUM AT  $25^\circ.7$

Pressure kg/cm <sup>2</sup>	$-\frac{1}{p} \frac{\Delta R}{R_0}$		Pressure kg/cm <sup>2</sup>	$-\frac{1}{p} \frac{\Delta R}{R_0}$	
	Increasing pressure	Decreasing pressure		Increasing pressure	Decreasing pressure
	0.00000	0.00000	15,000	190	247
0	200	310	20,000	190	233
5,000	195	286	25,000	198	222
10,000	192	265	30,000	211	211

The difference cannot be ascribed to the difference in range. The previous specimen showed no hysteresis, and presumably the present specimen would not have shown any either if the measurements had been confined to the 12,000 range, since the relation was almost linear with slight normal curvature in this range.

Lanthanum has been found<sup>17</sup> to have a polymorphic transition at 23,370 kg/cm<sup>2</sup> with a fractional volume change of 0.0036. No trace of any discontinuity in the resistance corresponding to this could be found in spite of the fact that readings were multiplied in the interval between 20,000 and 30,000 kg/cm<sup>2</sup>. Nevertheless it is natural to expect that the hysteresis in the resistance has some connection with this transition. Also to be considered in seeking for an explanation of the hysteresis is the fact that lanthanum crystallizes in the hexagonal system, so that the compressibility need not be the same in all directions. This effect is, however, presumably not large because the crystal system is the close-packed hexagonal arrangement and in general the difference of compressibility of such crystals in different directions is small.

*Cerium.* This metal is of particular interest because it has a transition with large volume change which occurs, according to X-ray measurements made at Chicago,<sup>18</sup> with no change in the lattice type, which is face-centered cubic for both modifications. The presumption is, therefore, that the transition is due to a rearrangement of the electronic shells. The theory has not been worked out, but for the only other known case of a similar transition, caesium, Sternheimer<sup>19</sup> has found by detailed calculation what the nature of the change in electronic orbit is. For caesium it is from a 6-f to a 5-d orbit.

I have previously made measurements on three specimens of cerium. The first was in 1923<sup>20</sup> on a specimen obtained from the General Electric Co. Compressibility measurements were made to 10,000 kg/cm<sup>2</sup>. The initial compressibility at 30° was  $35.74 \times 10^{-7}$  and the compressibility decreased with rising pressure as is normal for nearly all substances. The mean temperature coefficient of resistance between 0° and 100° was 0.001; from the low value of this coefficient I drew the conclusion at the time of the measurements that the purity was probably not high. The next measurements were in 1927<sup>21</sup> on material specially prepared by Dr. H. C. Kremers, who had specialized in the preparation of the pure rare earth metals, and stated that this specimen was free from other metals, and in particular iron, which is a usual impurity. The existence of a transition was found during the compressibility measurements and this was later verified by measurements on the electrical resistance. The electrical resistance measurements allowed a fairly good determination of the pressure of the transition, which was 7,600 kg/cm<sup>2</sup> at 30° and 9,400 at 75°. The transition was not perfectly sharp. The determinations of compressibility were confined to the range below 4,000 kg/cm<sup>2</sup> in order not to run into complications from the transition. In this range the compressibility was highly anomalous, increasing rapidly with increasing pressure. The initial compressibility at 30° was  $45.63 \times 10^{-7}$ . The electrical resistance of the low pressure modification increased linearly with pressure up to 3,000 with a mean coefficient of  $4.42 \times 10^{-6}$ . The resistance of the high pressure modification on the other hand decreases with rising pressure with a mean coefficient between 9,000 and 12,000 of  $-1.42 \times 10^{-5}$  in terms of the resistance at 9,000. The mean temperature coefficient of resistance between 0° and 100° was 0.00097, again abnormally low, and the specific resistance at 30°  $7.48 \times 10^{-5}$ . The third measurements were in 1948<sup>22</sup> on material obtained from MacKay of otherwise unknown origin and purity. This was used for measurements of compressibility to 40,000. A transition was found at 12,430 kg/cm<sup>2</sup> with volume change of 8 per

cent. This transition ran sharply. From this, and the fact that the previously measured transition was sluggish and the further fact that the first specimen had shown no transition at all, it was concluded that the present specimen was of greater purity than that obtained from Kremers. The high purity of the MacKay specimen was also suggested by its notable mechanical softness and easy extrusion. After the measurements had been published on the MacKay specimen, Lawson and collaborators at the University of Chicago published their results on the X-ray analysis under pressure. They found a transition in the neighborhood of 15,000 and with no change of lattice type, as already mentioned. Their cerium was obtained from the Atomic Energy Commission, freshly prepared with special emphasis on high purity. The presumption therefore was that the pressure of transition is sensitive to impurity, and is higher the higher the purity.

For the present measurements, the fourth time that I have measured cerium, I was fortunate to obtain some of the pure cerium of the Atomic Energy Commission, for which I am indebted to Dr. Spedding. This was not the very highest super material, which was available only for special purposes and with special permission, but the purity was understood to be high by ordinary standards. No quantitative analysis seems available. For the resistance measurements it was formed into wire 0.11 mm. in diameter by extrusion from a steel die at somewhat below a red heat. Extrusion was easy. The mean temperature coefficient of resistance at atmospheric pressure between 0° and 23° was 0.00087, and the specific resistance at 23°  $7.67 \times 10^{-5}$ .

The resistance measurements revealed the transition, with large change of resistance, but to my surprise at the lower pressure which had been formerly given by Kremer's specimen, rather than at the higher pressure suggested by the argument above. The higher pressures obtained at the University of Chicago must have been due to mechanical constraints on the specimen. Their pressures were not truly hydrostatic; the cerium was in the form of filings mixed with filings of a solid plastic to transmit pressure. It is known that a solid plastic under such conditions is capable of supporting very material stress differences.

The transition is not sharp and runs with hysteresis between increasing and decreasing pressure. Furthermore the width of the hysteresis loop is not always the same. The loop was described two times. The first time pressure was run to the full 30,000 before reversal, and the second time to only 8,000, at which there was a catastrophic drop of resistance. Many more readings were taken the second time, so that the cycle was described more slowly. The second time the cycle was narrower, the abrupt drop was greater, and

the recovery was more abrupt. These differences were probably a result of both the factors of difference—range of pressure and speed. It appeared probable that the cerium is not in a state of complete internal equilibrium, and at the suggestion of Dr. Cyril Smith of Chicago, the cerium was annealed by heating in vacuum to 400° C. and cooling over night in the furnace. This was repeated twice. Repetition of the resistance measurements showed no essential change. The discontinuity was at the same pressure and slightly less in amount; the initial slope of resistance versus pressure was unaltered. Above the transition the resistance dropped off slightly more rapidly with pressure after the annealing than before.

TABLE V  
CERIUM AT 23°.4

Pressure kg/cm <sup>2</sup>	$\frac{R}{R_0}$	Pressure kg/cm <sup>2</sup>	$\frac{R}{R_0}$
0	1.0000	10,000	.548
2,500	1.0104	15,000	.523
5,000	1.0200	20,000	.506
7,000	1.0272	25,000	.495
transition	.582	30,000	.487

The experimental points are shown in Figure 4. It is obvious that any formal tabulation of results from such curves can have only a limited significance. In Table V the results have been idealized by giving them single valued and with an abrupt drop. The pressure of the drop can be taken as 7,000 with some significance. On the second cycle there was an abrupt drop of resistance from 243 to 167 (arbitrary units) on increasing pressure from 7830 to 8020 kg/cm<sup>2</sup> and an abrupt rise from 187.1 to 233.5 on decreasing pressure from 5890 to 5740. Outside the transition zone the observed resistance was single valued, with no difference between increasing and decreasing pressure. Below the transition the resistance increases with pressure, but at a decelerating rate. This direction of curvature is abnormal; it is probably associated with the approaching transition. The same remark may be made about the abnormal curvature of the compressibility curve at low pressures. The mean pressure coefficient of resistance between atmospheric pressure and 2,500 kg/cm<sup>2</sup> is  $4.2 \times 10^{-6}$  against the value for Kremer's material  $4.4 \times 10^{-6}$ . The latter must have been nearly as pure as the present material. The pressure coefficient of the present material between 9,000 and 12,000 in terms

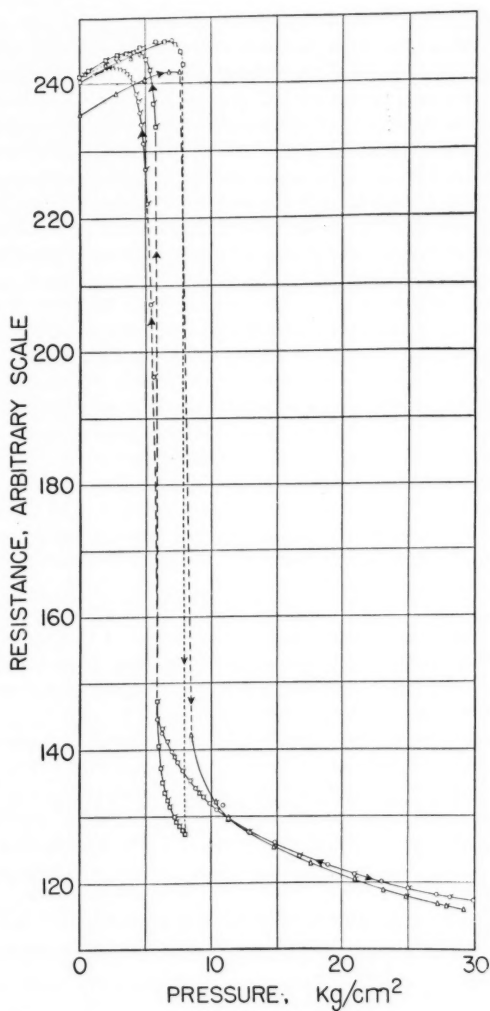


FIGURE 4. The resistance of cerium as a function of pressures. Different symbols indicate different runs. Symbols with wings indicate measurements with decreasing pressure.

of the resistance at 9,000 is  $-1.22 \times 10^{-5}$  against  $-1.42 \times 10^{-5}$  for Kremers. The agreement between the two specimens is closer than one would have thought possible in view of the character of the experimental points as shown in Figure 4.

The drop of resistance at the transition is by approximately 40 per cent of the value immediately before the transition. The drop is in the usual direction, resistance usually following volume. The measured drop of resistance includes the effect of changing dimensions when the transition runs. Because of the nature of the transition it is highly probable that the change of dimensions takes place uniformly in all directions. This would mean that the drop of specific resistance is somewhat greater on a percentage basis than the drop of measured resistance. If the change of volume is taken to be of the order of 8 per cent, assuming the values found at 12,000 for the specimen from MacKay, then the drop in specific resistance is 2.7 per cent greater than the drop in measured resistance. It is noteworthy that the initial resistance is exactly recovered after the cycle through the transition in spite of the large volume changes encountered. This again is presumptive evidence about the nature of the transition, which would appear to take place by a uniform contraction of the lattice equally in all directions. There are many other substances which show a consistent growth in some crystallographic direction on passing through a transition cycle.

*Praseodymium.* The material was obtained from MacKay a couple of years ago in massive form under oil. I formed it into wire 1 mm. in diameter by extrusion at a bright red heat from a die of special cobalt alloy for high temperature work with a high-speed steel piston in an atmosphere of nitrogen, which was so arranged as to stream around the issuing wire. Protection from the atmosphere during extrusion proved absolutely essential; extrusion into the air resulted in chemical action so rapid that the issuing metal melted. The former extrusion, in 1927 had not proved so difficult. The former metal<sup>23</sup> was obtained from Dr. H. C. Kremers and was known to be of high purity.

The electrical resistance shows no unusual features. The permanent change of resistance after the initial seasoning application of pressure was slight, and on the final run the points lay smoothly, with no hysteresis.  $-\frac{1}{p} \frac{\Delta R}{R_0}$  decreases nearly linearly with increasing pressure, but with slight convexity toward the pressure axis, the normal direction of curvature. In spite of the slowness of the curvature, a third degree expression in the pressure would not reproduce the results within experimental error.



The specific resistance at  $0^\circ$  of this specimen was  $7.39 \times 10^{-5}$  and the temperature coefficient between  $0^\circ$  and  $24^\circ$  0.00161. These figures are to be compared with  $6.9 \times 10^{-5}$  and 0.00165 respectively for the specimen of Dr. Kremers. The difference is not large and is in the direction to indicate inferior purity in the present specimen. There would seem little doubt, however, that the temperature coefficient of resistance of the pure rare earth metals is notably less than the 0.004 characteristic of all normal pure metals. The pressure coefficient of the present specimen is notably larger than that of the former, the mean value between atmospheric pressure and 10,000 kg/cm<sup>2</sup> now being  $-1.2 \times 10^{-6}$  against the former  $-2.4 \times 10^{-7}$ . The former specimen showed a very unusual dependence of pressure coefficient on temperature, the coefficient being more than three times as large at  $75^\circ$  as at  $24^\circ$ . The effect of temperature was not investigated in the present work.

*Neodymium.* The material was obtained from MacKay. It was extruded into wire 1.1 mm. in diameter in the same way as the praseodymium. Extrusion was somewhat more difficult than for praseodymium, it being necessary to heat somewhat hotter and push somewhat harder.

There is nothing noteworthy in the behavior of resistance under pressure. The permanent change of resistance on the initial application was almost undetectable.  $-\frac{1}{p} \frac{\Delta R}{R_0}$  against pressure is nearly linear, with slight curvature in the normal direction. Again, in spite of the slight curvature, a third degree equation would not reproduce the results. The general character of the results is not unlike those for praseodymium. The pressure coefficient of neodymium is somewhat larger numerically, and it drops off more rapidly with increasing pressure.

The specific resistance at  $0^\circ$  at atmospheric pressure was  $8.05 \times 10^{-5}$ , and the temperature coefficient of resistance at atmospheric pressure 0.00127 between  $0^\circ$  and  $24^\circ$ . Again we find a small temperature coefficient for a rare earth metal. Formerly, a temperature coefficient of 0.000799 was found.<sup>24</sup>

*Tantalum.* This was obtained in 1946 from the Fansteel Company, the purest which they were in a position to supply. Connection was by spring clips. The temperature coefficient of resistance at atmospheric pressure between  $0^\circ$  and  $24^\circ$  was 0.00367. This is materially higher than the coefficient 0.00297 of a specimen measured in 1917.<sup>25</sup>

The behavior of resistance under pressure shows no striking features.

The effect of pressure is small, with a very definite curvature of  $-\frac{1}{p} \frac{\Delta R}{R_0}$  in the abnormal direction.

The mean pressure coefficient of resistance to 10,000 kg/cm<sup>2</sup> was  $1.62 \times 10^{-6}$ , to be compared with  $1.44 \times 10^{-6}$  for the 1917 specimen. Both temperature and pressure coefficients of the two specimens differ in the direction which usually means higher purity in the present specimen.

*Tungsten.* This is the identical specimen that was used in 1932<sup>26</sup> for measurements down to liquid oxygen temperatures.

There is nothing noteworthy about the behavior to 30,000. There is perhaps more irregularity than usual at the low pressures, doubtless associated with the small absolute value of the coefficient. Above 10,000 the results lie smoothly enough, and there is no reason to assume anything other than a linear relation between  $-\frac{1}{p} \frac{\Delta R}{R_0}$  and pressure, the coefficient decreasing normally at high pressures.

The mean pressure coefficient at 24° to 10,000 kg/cm<sup>2</sup> is  $1.30 \times 10^{-6}$  to be compared with  $-1.25 \times 10^{-6}$  on another specimen in 1917.

*Iridium.* This was the identical specimen whose compressibility and electrical resistance were measured in 1923.<sup>27</sup> Its temperature coefficient of resistance was formerly found to be 0.00322, which is lower than the value 0.00361 in the literature, so that the purity could probably be improved.

The resistance to 30,000 shows no notable feature.  $-\frac{1}{p} \frac{\Delta R}{R_0}$  is linear with pressure, decreasing slightly at higher pressures as is normal. The average pressure coefficient of resistance over the first 10,000 kg/cm<sup>2</sup> is, according to the table,  $1.37 \times 10^{-6}$ , against the former value  $1.31 \times 10^{-6}$  over the same range. The initial coefficients are  $1.39 \times 10^{-6}$  and  $1.35 \times 10^{-6}$  respectively. The discrepancy increases at higher pressures, and is probably connected with the linear calibration of the manganin gauge formerly used.

*Platinum.* This was the same specimen that was used in 1932<sup>28</sup> in measurements of the effect of pressure on resistance down to liquid oxygen temperature. The leads were attached by soft soldering. The temperature coefficient at atmospheric pressure between 0° and 23° was 0.00394. The material was originally from Baker and Co., their purest.

Several applications of pressure were made before the final run, there being one or another difficulty with the apparatus. Platinum never settled down to as steady behavior as most of the other metals.

Even on the last run there was a slight irregularity of the zero, amounting to 1 per cent of the maximum pressure effect on increasing pressure. The pressure readings were smooth, and the results given in the table are extrapolated smoothly, disregarding the actual initial zero.

$-\frac{1}{p} \frac{\Delta R}{R_0}$  drops off nearly linearly with increasing pressure, but there is slight curvature in the abnormal direction.

The average pressure coefficient over the first 10,000 kg/cm<sup>2</sup> is practically identical with that found in 1917 on another specimen over the same range.

*CuZn.* This is the same specimen whose electrical resistance was measured to 12,000 kg/cm<sup>2</sup> in 1935.<sup>29</sup>

Nothing noteworthy is shown by the resistance to 30,000. There is some hysteresis, the difference of resistance with increasing and decreasing pressure at the mid point of the range amounting to one part in 125 of the maximum pressure effect. The values shown in the table are the average for increasing and decreasing pressure. The formerly measured values agree closely with the present ones. The former results, corrected to 23°, the temperature of the present measurements, for the initial coefficient and the average coefficient to 10,000 kg/cm<sup>2</sup> were  $-2.19 \times 10^{-6}$  and  $-2.07 \times 10^{-6}$  against the present values  $-2.194$  and  $-2.042 \times 10^{-6}$  respectively.

*AgZn.* This is the 1935 specimen,<sup>30</sup> with dimensions somewhat altered by filing to give greater geometrical regularity.

The resistance showed nothing noteworthy to 30,000. This also showed hysteresis, perhaps twice as much as the CuZn. The results in the table are the mean with increasing and decreasing pressure.

$-\frac{1}{p} \frac{\Delta R}{R_0}$  is approximately linear with pressure, decreasing with slight curvature in the normal direction (concavity toward the pressure axis). The 1935 measurements to 12,000, corrected to 24°, the temperature of the present measurements, gave for the initial pressure coefficient and the average coefficient over the first 10,000 kg/cm<sup>2</sup> the values  $-4.27 \times 10^{-6}$  and  $-3.85 \times 10^{-6}$  to be compared with the present values  $-4.13$  and  $-3.73 \times 10^{-6}$  respectively. The drop of the coefficient with rising pressure is larger than usual.

*AuZn.* This is the 1935 specimen.<sup>31</sup>

The resistance behaved perfectly smoothly to 30,000, with no perceptible hysteresis.  $-\frac{1}{p} \frac{\Delta R}{R_0}$  decreases linearly with increasing pressure.

The former measurements gave for the initial pressure coefficient and the average coefficient over the first 10,000 kg/cm<sup>2</sup>, corrected to 24°, the temperature of the present measurements, the values  $-3.53 \times 10^{-6}$  and  $-3.36 \times 10^{-6}$  against the present values  $-3.44$  and  $-3.27 \times 10^{-6}$  respectively.

*Cu<sub>5</sub>Zn<sub>8</sub> (Gamma Brass).* This was a new specimen, which I owe to the courtesy of Dr. Cyril Smith, who had it specially prepared at the Institute for the Study of Metals, University of Chicago. The material as furnished was in the shape of several cast rods 3.5 mm. in diameter. One of these was filed down to about 1 mm. in diameter for the resistance measurements. The other rods were destined for use in determining the tensile properties under pressure.

The temperature coefficient of resistance between 0° and 23° was 0.00287 and the specific resistance at 0°  $9.26 \times 10^{-6}$ . In 1935<sup>32</sup> measurements were made on two samples of ostensibly the same composition. One of these showed irregularities which were ascribed to incomplete internal equilibrium. The behavior of the other sample was smoother. For it the temperature coefficient of resistance and specific resistance were 0.00256 and  $9.92 \times 10^{-6}$  respectively.

The effect of pressure on the electrical resistance of the present specimen showed unusual features. On the initial seasoning application of pressure there was a 5 per cent permanent increase of resistance. The single seasoning application of pressure was apparently adequate, because on the next application of pressure there was no further change of resistance, neither was there any hysteresis between increasing and decreasing pressure. There was, however, a very noticeable anomaly at 5,000 kg/cm<sup>2</sup>. Up to this pressure resistance decreases with increasing pressure at a rapidly accelerating rate. At 5,000 there is a sharp cusp in the curve of  $-\frac{1}{p} \frac{\Delta R}{R_0}$  versus pressure, and above 5,000  $-\frac{1}{p} \frac{\Delta R}{R_0}$  decreases with increasing pressure as is normal, but with rather greater convexity toward the pressure axis than usual. The experimental values of  $-\frac{1}{p} \frac{\Delta R}{R_0}$  are shown in Figure 5, and the smoothed numerical results in Table VI.

The specimen measured in 1935 did not show any such anomaly. The initial pressure coefficient at 24°, the temperature of the present measurements, of this specimen was  $-1.46 \times 10^{-7}$  against  $-2.62 \times 10^{-6}$  for the present specimen. The material of the two specimens must be quite different.

*Ag<sub>5</sub>Zn<sub>8</sub>.* This was the 1935 specimen.<sup>33</sup>

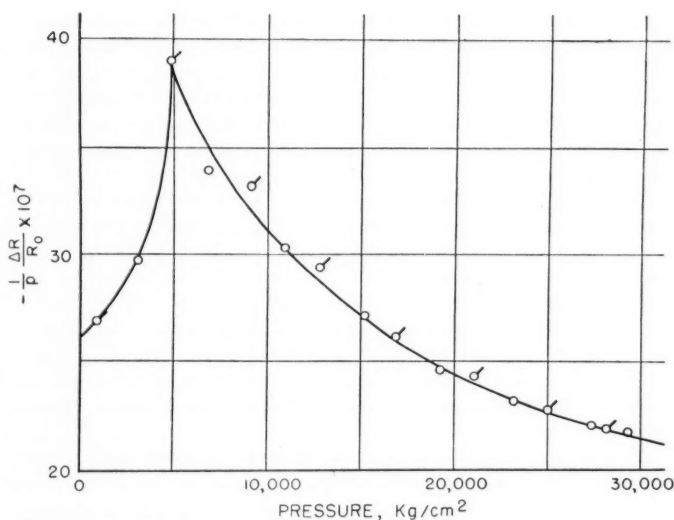


FIGURE 5. The experimental results for gamma brass. Circles with wings indicate measurements with decreasing pressure.

TABLE VI  
GAMMA BRASS ( $\text{Cu}_5\text{Zn}_8$ ) AT  $23^\circ.8$

Pressure kg/cm <sup>2</sup>	$-\frac{1}{p} \frac{\Delta R}{R_0}$	Pressure kg/cm <sup>2</sup>	$-\frac{1}{p} \frac{\Delta R}{R_0}$
0	0.00000	10,000	313
2,500	262	15,000	271
5,000	288	20,000	245
cuspl	386	25,000	226
		30,000	215

Under pressure there were neither seasoning effects nor hysteresis, but the results were unusual in that the resistance passes through a flat minimum in the neighborhood of 26,000 kg/cm<sup>2</sup>. This was verified by a repetition of the entire run with no change in the results.

Within the limits of error,  $-\frac{1}{p} \frac{\Delta R}{R_0}$  is linear in pressure, decreasing at 30,000 to less than half its initial value—whence the minimum. This means that the results can be written as a second degree expression in

pressure. Notice that the absolute value of the pressure effect is unusually small, which might suggest the nearness of a minimum.

When this specimen was measured in 1935 the results were very irregular with both creep and hysteresis. Within the large error of the measurements the change of resistance with pressure was linear up to 12,000. Furthermore, the temperature effects were very large, the average coefficient to 12,000 at 30° being  $-4.0 \times 10^{-7}$  and at 75°  $+10.4 \times 10^{-7}$ . The former resistance effect at 30° is thus not far from that found now. It would appear that during the fifteen years of rest since the former measurements this material has acquired approximate internal equilibrium.

*Ag<sub>2</sub>Al.* This was one of the specimens used in 1935,<sup>34</sup> the one for which results were published for the effect of pressure on resistance to 12,000 kg/cm<sup>2</sup> and designated as No. 2. It was found possible to attach leads to the specimen for the present measurements by soft soldering, although previously it was thought that soldering was not possible and spring clips were used.

The pressure effects on resistance to 30,000 are smooth, with neither permanent change of resistance nor hysteresis. The effects are unusual in that the resistance increases with pressure and at a rapidly accelerating rate.  $+\frac{1}{p} \frac{\Delta R}{R_0}$  against pressure is linear, rising from an initial value of  $5.0 \times 10^{-8}$  to  $16.3 \times 10^{-8}$  at 30,000. Measurements to 12,000 fifteen years ago on the same specimen gave similarly very small absolute values for the coefficients. As with Ag<sub>5</sub>Zn<sub>8</sub>, there was a reversal of sign of the coefficient on passing from 30° to 75°, but in the opposite direction, the coefficient at 30° being  $+10.1 \times 10^{-8}$  and at 75°  $-17.5 \times 10^{-8}$ . The coefficients were independent of pressure. These measurements were uncertain from creep and hysteresis. Again, during the fifteen intervening years the material seems to have settled down to steady behavior.

*Sb<sub>2</sub>Tl<sub>7</sub>.* This was the 1935 specimen.<sup>35</sup> There had been some surface chemical action over the years, the surface being covered with a white powder. The specimen was cleaned down to sound metal with emery paper, and connection made with spring clips.

The pressure effects show nothing unusual. There was neither permanent change of resistance nor hysteresis.  $-\frac{1}{p} \frac{\Delta R}{R_0}$  decreases with increasing pressure with slight convexity toward the pressure axis, as is normal. The initial pressure coefficient given by the former measurements to 12,000, corrected to 26.3°, the temperature of the present measurements, was  $-9.16 \times 10^{-6}$  against the value

— 9.58 found now. The difference is beyond any possible experimental error, and would point to some small internal change in the specimen.

*Carbology.* The measurements on this material were made in a spirit of curiosity, perhaps idle, the material being at hand and it being conceivable that at some time the coefficient might be useful in the construction of pressure apparatus. The specimen was of grade 999 carbology, the grade with the minimum binder and of composition WC 97, Co 3, as described by the Carbology Co. It was a slender rod 1.5 mm. in diameter and 4 cm. long, one of a number of similar rods from which pistons were cut for my 100,000 piezometers.

The specific resistance at  $0^\circ$  was  $4.88 \times 10^{-5}$  and the mean temperature coefficient of resistance between  $0^\circ$  and  $23^\circ$  0.00494. This latter is higher than would be anticipated for this class of material, being more like the value to be expected for a pure metal.

Before the regular pressure run a seasoning application of 30,000 kg/cm<sup>2</sup> was made. Any permanent change of resistance that may have been the result of this first application of pressure was too small to disentangle from the effect of temperature drift during the run. The results for the regular pressure run were smooth, without hysteresis or permanent change of zero. Resistance decreases under pressure

and  $-\frac{1}{p} \frac{\Delta R}{R_0}$  decreases with increasing pressure, as is normal. The

results were unusual, however, in the very large curvature, particularly at the low pressures, of  $-\frac{1}{p} \frac{\Delta R}{R_0}$  against pressure. A large initial

effect and a rapid decrease with pressure might be anticipated in view of the structure of this material in terms of grains sintered together, such an effect being interpreted as due to an initial pushing of the grains into closer contact with exhaustion of the effect at higher pressures. Such a picture, however, would lead one to expect permanent changes on the first application of pressure, and there was no

trace of any such. Above 15,000 kg/cm<sup>2</sup>,  $-\frac{1}{p} \frac{\Delta R}{R_0}$  becomes sensibly

linear in pressure with only a comparatively small rate of decrease. There is no suggestion whatever from present data that the resistance will ever pass through a minimum, in spite of the abnormally rapid

initial drop of  $-\frac{1}{p} \frac{\Delta R}{R_0}$ .

## DISCUSSION AND SUMMARY

All the metals and intermetallic compounds measured here except  $\text{Ag}_2\text{Al}$  are "normal" with respect to the effect of pressure on resistance in that the resistance decreases with increasing pressure. A number of metals with "abnormal" positive pressure coefficients of resistance have been previously measured over the 30,000 range. A discussion of the results on the metals measured here can therefore give only a partial picture of the whole range of the pressure phenomena.

Nearly all the metals and compounds measured here follow a rather simple pattern. Their resistance decreases under pressure, but at a decreasing rate at higher pressures, so that the curve of total resistance against pressure is convex toward the pressure axis. For eleven of these, namely for Al, Co, Zr, Cb, Mo, Rh, Pd, W, Ir,  $\text{AuZn}$  and  $\text{Ag}_5\text{Zn}_8$ ,  $-\frac{1}{p} \frac{\Delta R}{R_0}$  decreases linearly with increasing pressure.

This means that the resistance may be expressed as of the second degree in the pressure. A comparison of the relation between resistance and pressure with the relation between volume and pressure shows that in all cases the relative curvature is several fold greater for the resistance than for the volume. Of the pure metals the curvature is notably large for aluminum and zirconium. For the latter it is so large that a linear extrapolation would indicate a minimum resistance at 35,000  $\text{kg}/\text{cm}^2$ . A minimum resistance has up to now been actually realized only for caesium, rubidium, and potassium. Of the intermetallic compounds of this paper the curvature is so great for  $\text{Ag}_5\text{Zn}_8$  that the minimum is actually realized at 26,000  $\text{kg}/\text{cm}^2$ . For the exceptional compound,  $\text{Ag}_2\text{Al}$ ,  $\frac{1}{p} \frac{\Delta R}{R_0}$  is linear in pressure, and rapidly increases with rising pressure, which means that resistance rises at an unusually high rate at higher pressures. The significance of this abnormal effect for  $\text{Ag}_2\text{Al}$  is obscured by the absolute smallness of the pressure coefficient, and the fact that the sign reverses at higher temperatures.

For ten of the remaining substances  $-\frac{1}{p} \frac{\Delta R}{R_0}$  is *nearly* linear with pressure and in all cases the deviation from linearity is in the same direction, namely  $-\frac{1}{p} \frac{\Delta R}{R_0}$  drops less rapidly at the higher pressures. These ten substances are: Mg, Be, Ti, In, Pt, Nd, Pr,  $\text{CuZn}$ ,  $\text{AgZn}$ , and  $\text{Sb}_2\text{Te}_3$ . For a number of them the curvature is so slight that a third degree expression in the pressure will reproduce the relation



between resistance and pressure within experimental error. For several of the others a third degree expression will not suffice; the details have been given under the discussions of the individual substances. For carbonyl the relation between  $-\frac{1}{p} \frac{\Delta R}{R_0}$  and pressure exhibits unusually large curvature which is mostly confined to the low pressure end of the range, the curve rapidly flattening out at the high pressure end. Tantalum is unusual in that the curve of  $-\frac{1}{p} \frac{\Delta R}{R_0}$  against pressure at first rises and then falls. This means that resistance against pressure at first falls with increasing slope, but then there is a point of inflection beyond which the curvature reverses and becomes normal.

This leaves only a few markedly "abnormal" substances, Cr, Ni, La, Ce, and  $\text{Cu}_5\text{Zn}_8$ . Cerium experiences a first order phase change at 7,000 kg/cm<sup>2</sup> with unusually large volume change. At this transition resistance drops, following the change of volume, which is the usual direction of resistance change at a transition. Above the transition the resistance of cerium decreases normally with pressure and with normal curvature. Below the transition its resistance increases abnormally with pressure and with abnormal curvature for an increasing resistance. The precise details of the transition including the pressure at which it runs and hysteresis of the transition, are somewhat obscured by different results obtained with specimens from different origins. The effects are probably impurity effects but if so they are somewhat unusual. The abnormality in lanthanum consists in an unusually large hysteresis between resistance with increasing and decreasing pressure. Lanthanum is known<sup>36</sup> to have a first order transition at 23,370 kg/cm<sup>2</sup>. No trace of this was found in the resistance measurements. It may have been that it was suppressed because of the smallness of the resistance specimen. It may be mentioned in this connection that there is a cusp in the relation between volume and pressure<sup>37</sup> of palladium at 16,500 kg/cm<sup>2</sup> of which there was not the slightest trace in the resistance relation.

This leaves three abnormal substances, Cr, Ni, and  $\text{Cu}_5\text{Zn}_8$ , all of which have a cusp in the relation between resistance and pressure.

Below the pressure of the cusp  $-\frac{1}{p} \frac{\Delta R}{R_0}$  increases (abnormally) with rising pressure, and above it, decreases. In the case of nickel the cusp occurs at the same pressure, 10,000 kg/cm<sup>2</sup>, as the previously found cusp in the volume pressure relation.<sup>38</sup> For the other two substances no cusp was found in previous measurements of volume. However,

there were abnormalities in the volume relations which were not reflected in the behavior of resistance. But these previous measurements were not made on the identical specimens, and it appears that the behavior of these two substances is unusually sensitive to small differences of purity or handling, since consistent results on different specimens were not obtained in the volume measurements.

I am indebted to Mr. L. H. Abbot for making the readings for this paper.

LYMAN LABORATORY OF PHYSICS,  
Harvard University, Cambridge, Mass.

## REFERENCES

1. P. W. Bridgman, Proc. Amer. Acad. 72, 157-205, 1938.
2. P. W. Bridgman, Proc. Amer. Acad. 70, 71-101, 1935.
3. P. W. Bridgman, Proc. Amer. Acad. 74, 1-10, 1940.
4. P. W. Bridgman, Proc. Amer. Acad. 52, 573-646, 1917.  
56, 61-154, 1921.  
58, 151-161, 1923.  
59, 109-115, 1923.  
60, 385-421, 1925.  
62, 207-226, 1927.  
63, 329-345, 1928.  
63, 347-350, 1928.  
64, 51-73, 1929.  
64, 75-90, 1930.  
66, 255-271, 1931.  
67, 29-41, 1932.  
67, 305-344, 1932.  
68, 27-93, 1933.  
68, 95-123, 1933.  
70, 285-317, 1935.
5. P. W. Bridgman, Proc. Amer. Acad. 77, 190-234, 1949.
6. Twelfth reference under (4).
7. Fifteenth reference under (4).
8. Fourteenth reference under (4).
9. Thirteenth reference under (4).
10. Seventh reference under (4).
11. Eighth reference under (4).
12. Thirteenth reference under (4).
13. Thirteenth reference under (4).
14. Thirteenth reference under (4).
15. Ninth reference under (4).
16. Sixth reference under (4).
17. P. W. Bridgman, Proc. Amer. Acad. 76, 75, 1947.
18. A. W. Lawson and Tang Ting-Yuan, Phys. Rev. 76, 301, 1949.

19. R. M. Sternheimer, *Phys. Rev.* 75, 888, 1949.
20. P. W. Bridgman, *Proc. Amer. Acad.* 58, 199, 1923.
21. Sixth reference under (4).
22. P. W. Bridgman, *Proc. Amer. Acad.* 76, 75, 1948.
23. Sixth reference under (4).
24. Second reference under (4).
25. First reference under (4).
26. Thirteenth reference under (4).
27. Third reference under (4).
28. Thirteenth reference under (4).
29. Sixteenth reference under (4).
30. Sixteenth reference under (4).
31. Sixteenth reference under (4).
32. Sixteenth reference under (4).
33. Sixteenth reference under (4).
34. Sixteenth reference under (4).
35. Sixteenth reference under (4).
36. P. W. Bridgman, *Proc. Amer. Acad.* 76, 75, 1948.
37. Reference (5), p. 204.
38. Reference (5), p. 203.

180✓

